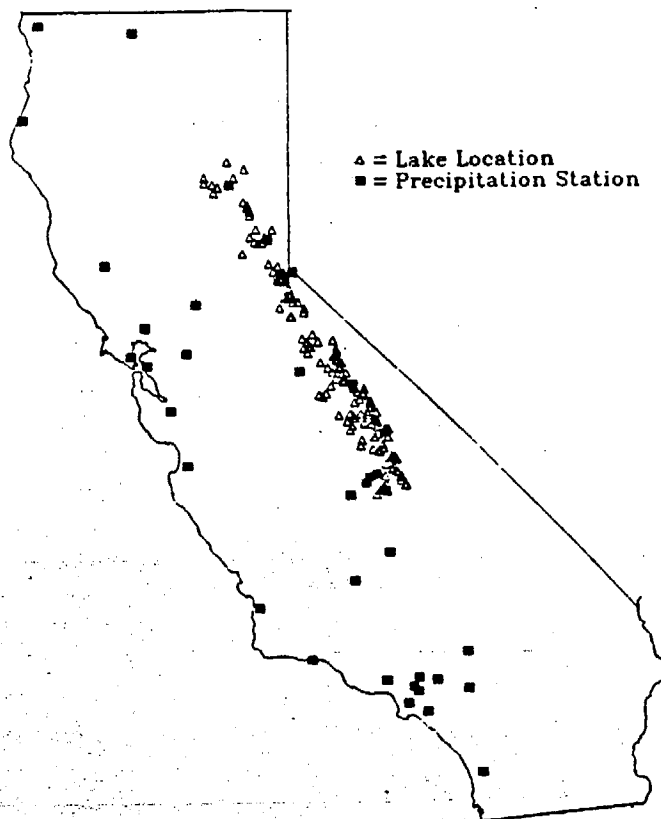Final Report

Steady State Model to Determine Lake Resources at Risk to Acid Deposition in the Sierra Nevada, California

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△ = Lake Location
■ = Precipitation Station

ABSTRACT

Lakes in the Sierra Nevada of California are sensitive to increased acid deposition due to high elevation, poorly buffered soils, and granitic geology. A simple charge balance equation was used to predict the acid neutralizing capacity (ANC) which would occur in the watersheds of 198 lakes in the Sierra based on current lake and deposition chemistry. Changes in ion concentrations were studied for different scenarios of acid deposition (wet and dry). Currently, 28.5% of the study lakes have a Gran alkalinity of 40 μeq/L or less. Lakes in this range are considered to be sensitive to increased acid loadings.

Three scenarios were used in this study. The first scenario considered changes in deposition sulfate only. It was assumed that changes in acid were due only to sources of sulfuric acid and sulfur dioxide. The second scenario used changes in deposition of ammonium nitrate. The third scenario was a combination of the first two assuming that their contributions to the change in alkalinity were additive. Each scenario was studied at double and half of the current levels of deposition input to the watershed.

Sulfuric acid loadings at twice the current levels resulted in an increase in sensitive lakes of approximately seven percent. More importantly, 1.2% of the lakes resulted in ANC values less than zero. Loadings at half the current levels had a less effective result. The percentage of sensitive lakes under this loading decreased only 2.7%.

The effect of increased ammonium nitrate deposition was smaller relative to increases in sulfuric acid deposition. Ammonium nitrate results in an acidifying influence because most all of the ammonium is taken up or nitrified in the watershed (an acidifying influence), while, on the average, 93 percent of nitrate is taken up or reduced (an alkalizing effect).

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The net result is slightly acidifying. The percentage of sensitive lakes increased only five percent for an increase of 100% in deposition of ammonium nitrate with no lakes becoming acidic. A 50% decrease in loadings resulted in a drop of 1.7% in the number of sensitive lakes. This is for a 1:1 ratio of NH_4^+/NO_3^- in deposition. The model is sensitive to this ratio in deposition. Due to biological reactions, a ratio of ammonium to nitrate greater than 1:1 will result in a greater acidification effect on surface waters.

Combined changes in sulfuric acid and ammonium nitrate loadings have the greatest overall effect. The number of sensitive lakes for a 100% increase in loadings rose nine percent, with 2.5% of the lakes becoming acidic. Half the current loading levels resulted in a decrease of 5.6% of the number of sensitive lakes. Again, the ratio of NH_4^+/NO_3^- can become very important for values greater than 1.0.

ACKNOWLEDGEMENTS

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

It has been reported that many parts of the world currently receive acid deposition. Many of those regions have shown the effects of such exposure by an increase in the number of acidic lakes and the loss of biota in such lakes. The Sierra Nevada in California is one of those regions that have been reported as sensitive and receiving low levels of acid deposition. The characteristics of watersheds and lake waters in the alpine zone are similar to those in other regions in the world that contain acidified lakes. This would indicate that the watersheds and lakes in this region might also be at risk to further inputs of acid deposition. There is evidence of episodic acidification in lakes and streams in the southern Sierra (Melack et al. 1987; Dozier et al. 1987).

The University of Iowa (UI) database was formed in order to provide a population of lakes in the Sierra Nevada that could be used to determine their present chemical condition and to determine what percentage of lakes that would be at risk should acid loadings increase. Results obtained from the manipulation of data in the UI database and the Environmental Protection Agency's Western Lake Survey can be used to scale-up and determine the population of lakes at risk to acidic deposition. Conclusions based on the analysis of this database are as follows:

1. There is a large percentage of sensitive lakes (ANC < 40 μeq/L) in the Sierra Nevada in California. There are currently no acid lakes. Relative to the eastern United States, the amount of acid deposition is not great. Wet acid deposition is greater than dry deposition.

2. Henriksen's nomograph was not accurate in determining the present number of sensitive (ANC < 40 μeq/L) lakes. This indicates that the data used to empirically develop this model may not accurately describe lakes in the Sierra. It may also indicate that the amount of nitrogen sources of acid in deposition are substantial. The Henriksen nomograph only considers deposition of sulfate sources of acid. Regions which receive significant amounts of nitrogen deposition will not be accurately described by this model. Therefore, the use of Henriksen's nomograph as a predictive model in the Sierra Nevada is not advised.

3. The steady state charge balance model was developed as a means of predicting the percentage of sensitive and acid lakes that will result for changes in deposition loadings of sulfuric acid, ammonium nitrate, and a combination of both. These species were chosen by CARB after performing factor analysis on precipitation data collected at Emerald Lake and Giant Forest in Sequoia National Park. The results of steady state charge balance model are summarized in Table 8.

Sulfuric acid loadings at twice the current levels resulted in an increase in sensitive lakes (ANC < 40 μeq/L) of approximately seven percent. More importantly, 1% of the lakes showed ANC values less than zero. Loadings at half the current levels had a less dramatic result. The percentage of lakes in the sensitive category under this loading decreased only 3%.

The effect of increased ammonium nitrate deposition is smaller relative to increases in sulfuric acid deposition. Ammonium nitrate deposition results in an acidifying influence because most all of the ammonium is taken up or nitrified in the watershed (an acidifying influence), while, on the average, 93 percent of nitrate is taken up or reduced (an alkalizing

effect). The net result is slightly acidifying. The percentage of sensitive lakes increased only five percent with no lakes becoming acidic. A 50% decrease in loadings resulted in a decrease of 2% in the number of sensitive lakes for a 1:1 ratio of NH_4^+/NO_3^- in deposition. The model is sensitive to this ratio in deposition. It also does not take into account the effect of reductions in NH_3 emissions in the Central Valley that might allow nitric acid to be transported.

Combined changes in sulfuric acid and ammonium nitrate loadings have the greatest overall effect on lake chemistry. The number of sensitive lakes for a 100% increase in loadings rose nine percent with 3% of the lakes becoming acidic. Half the current loading levels resulted in a decrease of 6% of the number of sensitive lakes. Again, the ratio of NH_4^+/NO_3^- can become very important for values greater than 1.0.

The cases for wet and dry precipitation years were also studied. In the case for each of the three scenarios discussed, a greater number of lakes become sensitive for the case of a dry year as opposed to a wet year. This is due to the greater extent of concentration of acid-associated ions in the dry year.

Recommendations

1.   Better quality data are required for a detailed uncertainty analysis to be performed. This includes improvements in wet and dry deposition chemistry, improved methods of extrapolating wet deposition chemistry and snow pack chemistry to lakes in the database, better prediction of future trends in NH_4^+/NO_3^- deposition, and improved values of the evapoconcentration factors at each lake.

2.   Future episodic scenarios, as well as current events, must be considered with better event models. This could be possible with data from the four lake watersheds under

intensive study in the southern Sierra. The 102 lakes from the EPA's Western Lake Survey may be an adequate source of data if inclusion probabilities are provided.

3. Snowmelt events are potentially more important in terms of acidification than summer deposition events. Many lakes experience low pH and low ANC, but current levels of acidic deposition are not sufficient to chronically acidify the systems. It would therefore be useful to include UCSB's snowmelt formulations in the event model as well.

4. The Air Resources Board should use this regional assessment to (1) estimate the resources at risk to chronic acidification, (2) devise a field program to provide better data for both episodic and chronic acidification models, (3) to use this kind of analysis as a basis for considering deposition standards, and (4) to establish source-receptor relationships in order to relate proposed emission standards to aquatic effects at sensitive receptors for future modeling efforts.

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CHAPTER I

INTRODUCTION

Significance of Acid Deposition

The phenomenon of acid deposition has been recognized by scientists and governments to be one of the most pressing environmental issues facing large regions of eastern North America, western Europe and Scandanavia (Ontario Ministry of the Environment 1980). The effects of this phenomenon have been documented as early as the mid-seventeenth century. Cowling (1982) compiled an historical resume of noted works which details the observations of scientists related to air pollution and its effects. Cowling noted that an Englishman, Hales, in 1727 reported that dew and rain were acidic "for the air is full of acid and sulphureous particles..." Only recently has attention focused on the effects of acidic deposition on human health and the environment.

Watersheds that are characteristically sensitive to inputs of acid deposition face decreases in pH that may affect the biota in the area. Acidification of lakes in southern Norway have lost fish populations and have reduced rates of organic decomposition (Likens 1979). Fish in sensitive lakes in Canada have reduced reproduction capabilities. Loss of fisheries have also been observed (Beamish 1976). These watersheds are generally situated on bedrock types that are highly resistant to weathering thus reducing the concentrations of basic cations in surface waters. These waters typically have low buffering capacities (the ability to neutralize inputs of acids) and allow lakes and streams to become acidified as inputs of acid deposition continue.

Acid deposition has been shown to affect growth patterns of vegetation and other biomass (EPA 1983). The effects of acid deposition are also of major concern in the areas

of human health and the effects on wildlife. Damage to buildings and other man-made structures has also been attributed to acid deposition (Bubenick 1984; Ashbaugh et al. 1988).

The major chemical components that are the cause of the acidification of rain and snow (wet deposition) and particulate matter and gases (dry deposition) are oxides of sulfur and nitrogen. Compounds of each of these substances have long been produced by natural processes, such as volcanism, the activity of soil bacteria, and the decomposition of organic matter. The environment is capable of neutralizing small additions of acid through natural processes (Mohnen 1988). Precipitation preserved in glaciers and continental ice sheets that fell before the Industrial Revolution has been found to have a pH generally above 5.0 (Likens et al. 1979). The pH of rain and snow in the presence of normal concentrations and pressures of carbon dioxide in unpolluted atmospheres would be 5.6. However, the extensive use of fossil fuels as an energy source since the Industrial Revolution has greatly increased the amounts of sulfur and nitrogen oxides released into the atmosphere. These increases have overwhelmed nature's acid neutralizing processes resulting in the acidification of surface waters in some areas of the world. It is estimated that on an annual basis the rain and snow that fall over large areas of the world are currently up to five to fifty times more acidic than this lowest expected value (Likens et al. 1979). Figure 1 shows the genesis of acid precipitation.

Under normal, unpolluted conditions, an equilibrium is established between surface waters and the naturally-occurring carbon dioxide (CO_2) in the atmosphere. The carbon dioxide enters the watershed as carbonic acid (H_2CO_3) in precipitation and, together with H_2CO_3 from soil respiration, reacts with the calcium carbonate ($CaCO_3$) in soils and minerals according to Equation 1.
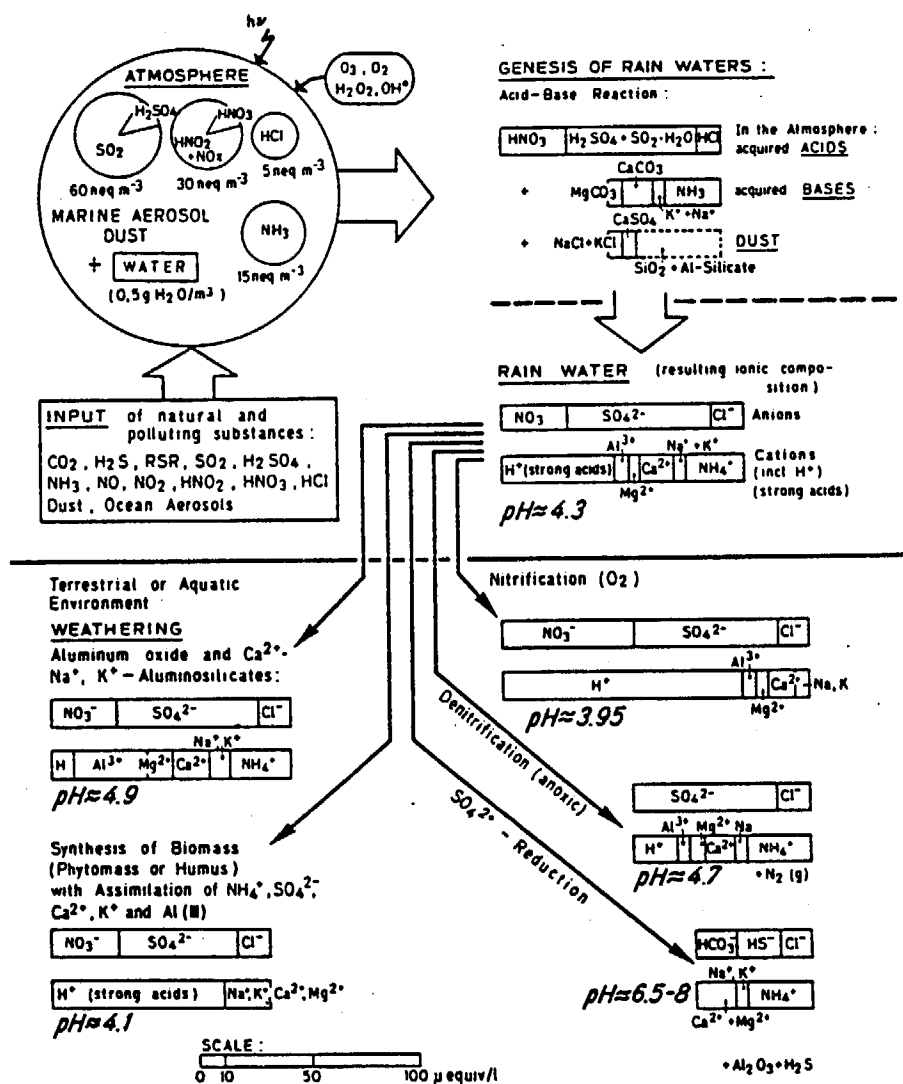
Figure 1. The genesis of acid precipitation (Schnoor and Stumm 1985)

$$CaCO_{3(s)} + H_2CO_{3(aq)} \iff Ca^{2+} + 2HCO_3^- \qquad (1)$$
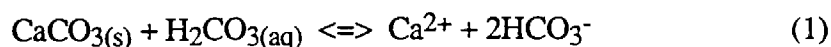
It is in this way that mineral weathering of calcareous minerals (those containing $CaCO_3$) neutralizes naturally-occurring inputs of acid.

The input of sulfur and nitrogen oxides into the atmosphere through the combustion of fossil fuels has created an abundance of sulfuric (H_2SO_4) and nitric (HNO_3) acid as shown in Equations 2 and 3. Minerals such as calcite are dissolved and the hydrogen ion acidity is neutralized.

$$CaCO_{3(s)} + H_2SO_{4(aq)} \iff Ca^{2+} + H_2CO_{3(aq)} + SO_4^{2-} \qquad (2)$$

$$CaCO_{3(s)} + HNO_{3(aq)} \iff Ca^{2+} + HCO_3^- + NO_3^- \qquad (3)$$
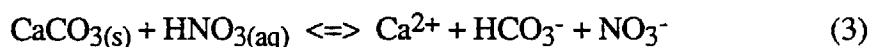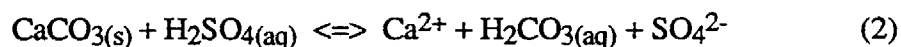
The reaction in Equations 2 and 3 are not as favored chemically and the reaction in Equation 1 dominates until all the sulfuric and nitric acid has been consumed. In the reaction in Equation 2, no alkalinity (HCO_3^-) is produced. Alkalinity generating capacity is what neutralizes inputs of acid. The amount of alkalinity in a lake is defined as its acid neutralizing capacity (ANC). When this value reaches zero the lake is termed acidic. It is through the reaction shown in Equation 2 and the lack of alkalinity production that leads to lakes becoming acidic or sensitive to acid inputs.

The sulfur and nitrogen compounds emitted into the atmosphere are often carried thousands of miles from their sources. This long travel time allows for more complete chemical conversion of these compounds into their acidic forms (Oak Ridge National Laboratory 1988). Thus areas which are most affected by acidic deposition are found to be in fairly remote areas from the populated and industrialized areas. Acid lakes have been

reported in Norway (Wright et al. 1976), Canada (Beamish 1976), and the in the northeastern (Likens et al. 1979 and Driscoll and Newton 1985) and upper midwest portions of the United States (Schnoor et al. 1986).

Importance of Studying Lakes in the Sierra Nevada

The Environmental Protection Agency initiated the National Surface Water Survey in an effort to determine the number of acidic and acid sensitive lakes in the United States. The Eastern Lake Survey (Linthurst et al. 1986) was conducted in 1984 and its western counterpart, the Western Lake Survey, was conducted in 1985 (Landers et al. 1987). Acid neutralizing capacity values at the 20th percentile were lower for lakes in the Eastern Lake Survey. However, median ANC values for lakes in the Western Lake Survey were lower than for those in the east (Eilers et al. 1987a). Therefore, since a number of lakes in the northeastern U.S. are currently acidic, it is quite possible that lakes in the western U.S. may also become acidic if inputs of acid deposition to these watersheds continue at current or increased levels.

The State of California recognized this possibility and also the potential for adverse health effects by passing legislation to study acid deposition and its effects. The Kapiloff Acid Deposition Act, passed in 1982, required the California Air Resources Board to set up a comprehensive research and monitoring program to investigate acid deposition in the state. A part of this program concentrated on the effects on the natural environment including the alpine lakes and streams of the Sierra Nevada (Ashbaugh et al. 1988). The California State Legislature has also passed the Atmospheric Acidity Protection Act in 1988. This law requires the Air Resources Board to continue its current research and to consider standards to protect health and welfare in California.

One concern of the State of California is to protect Sequoia and Yosemite National Parks and Forest Service wilderness areas from further environmental effects (no significant deterioration). This report specifies that number of acid lakes that can be expected under various acid deposition scenarios. It is a steady state approach and in the absence of any increase in acid deposition, chronic acidification of lakes is not expected. However, episodic acidification may occur and future research will focus on such events. Source-receptor relationships will need to be established in order to relate proposed emission standards to aquatic effects at sensitive receptors. Emission projections will be required for future modeling efforts.

Objectives

The alpine watersheds in the Sierra Nevada are among the most weakly buffered in the world and are very sensitive to the effects of acid deposition (Dozier et al. 1987). The monitoring of precipitation throughout the state of California records many locations receiving acid deposition (CARB 1988b). There is a large number of lakes in this mountain range.

The purpose of this research was to conduct a regional assessment of lakes in the Sierra Nevada and to:

(1) Determine the percentage of lakes in the Sierra Nevada that are sensitive to further inputs of acidic deposition.

(2) Determine the number of lakes which may become acidic (ANC ≤ 0) or may become sensitive (ANC < 40 μeq/L) due to increases in the current levels of deposition under various loading scenarios using empirical and steady state models.

(3) Determine the number of lakes which may become less acidic or may become less sensitive due to decreases in the current levels of deposition under various loading scenarios using empirical and steady state models.

(4) Understand and quantify the biogeochemical processes of greatest importance in controlling the acid-base chemistry of lakes in the Sierra Nevada.

CHAPTER II

LITERATURE REVIEW

Other Regional Studies

Regional studies have been conducted for lakes in the northeastern (Driscoll and Newton 1985; Schnoor et al. 1986a) and upper midwest (Schnoor et al. 1986b), portions of the United States, Canada (Beamish 1976) and Norway (Wright et al. 1979). A number of acid lakes have been reported in each of these areas. Table 1 shows the percentage of acidic ($ANC < 0$ $\mu eq/L$) and sensitive ($ANC \leq 50$ $\mu eq/L$) lakes in various regions of the United States (Schnoor 1987). These studies had defined sensitive lakes as those lakes with $ANC \leq 50$ $\mu eq/L$ which differs from the definition of 40 $\mu eq/L$ that will be used for the results of this report. The pH of precipitation in these regions ranges from about 4.0 to 4.5.

Characteristics of Acid-Sensitive Lakes

The basic processes which neutralize acid inputs to lake watersheds are mineral weathering and ion exchange. These processes occur in the soils and bedrock of the watersheds and can prevent surface waters from losing ANC (EPA 1983). Mineral weathering is the process by which inputs of acid chemically react with rocks and minerals. This reaction results in the consumption of hydrogen ions (H^+) and the release of basic metal cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) present in minerals. Ion exchange is the process of exchanging acid cations with basic metal cations present in the soil as a result of the mineral weathering process. The extent to which each process takes place depends on the characteristics of the watershed, such as its geology, amount of vegetation and flow paths.

Table 1. Approximate percentage of lakes (by number) that are presently acidic or sensitive to increased acid deposition in various regions of the United States (Schnoor 1987).

Region	ACID LAKES Percentage of Lakes with $ANC < 0$ µeq/L	SENSITIVE LAKES Percentage of lakes with $ANC \leq 50$ µeq/L
Northeast	5	15
Upper Midwest	2	8
Southern Blue Ridge	0	1
Florida	22	35
Sierra Nevada	0	38

Watersheds with alkaline soils, such as those rich in limestone, can easily neutralize acid deposition through ion exchange. Similarly, watersheds that are underlain by bedrock that is easily weatherable, such as limestone and other calcareous minerals, can supply a large amount of exchangeable metal cations to the soil through mineral weathering.

The amount of vegetation and the flow paths of direct precipitation and snowmelt runoff also affect the ion exchange process. Large areas of vegetation can disrupt overland flow such that it may seep into the soil layer where ion exchange occurs. Precipitation which flows directly over the watershed without much interaction with the soil cannot be completely neutralized. Watersheds with large areas of exposed bedrock have short contact time between precipitation and rock and soil. This prevents any appreciable amount of weathering from taking place.

Lakes in the northeastern United States are susceptible to the effects of acid deposition due to the small amount of weathering which takes place in their granite-based bedrock. This leaves the surrounding soil very weakly buffered due to a lack of metal cations that would be produced in chemical weathering reactions (Driscoll and Newton 1985). Sensitive areas such as these also lack the ability to retain inputs of acid anions (SO_4^{2-}, Cl^-, NO_3^-) in the soil. These anions flow directly into surface waters. Due to electroneutrality this input of anions must be accompanied by an equivalent input of cations. The absence of metal cations in these watersheds leaves only the acid hydrogen cation, H^+, to satisfy this condition. Chronically acidified lakes in the northeast cannot support fisheries (Kelso and Gunn 1984).

<u>Sensitivity of Lakes in the Sierra Nevada</u>

Acid Deposition in the Sierra Nevada

The Sierra Nevada is located directly east from one of the the two most populated areas of California. The San Francisco Bay Area and the Central Valley are major sources of nitrogen oxides due to the large number of automobiles present there and sulfur oxides from power plants. A source of sulfur oxides is the petrochemical production and refining operations in the Bakersfield area. Ammonium, another input that can lead to watershed acidification as will be discussed later, is derived from the agricultural activities in the Central Valley. These sources contribute compounds to the atmosphere where they undergo chemical reactions and are converted to acidic forms. The compounds eventually find their way to the Sierra where they are deposited in either wet or dry forms. Approximately 90% of precipitation in the alpine zone of the Sierra falls as snow with a pH of 5.4 (Dozier et al. 1987). However, Melack et al. (1982) reported acid rain with pH values ranging from 3.7 to 4.9 during storms in the east central Sierra during the dry season of 1981. These rains contained high concentrations of ammonium, nitrate and sulfate.

Characteristics of Watersheds in the Sierra Nevada

Watersheds in the Sierra Nevada are underlain by a granitic bedrock and contain thin, poorly-buffered soils (Tonnessen and Harte 1982). The watersheds also contain large areas of exposed bedrock and very little vegetation. The fact that the watersheds in the area are geologically young explains why the soils are so poorly buffered. There has not been sufficient time for the development of the soils that buffer inputs of acids. The typically small watershed areas and the dilute and low alkalinity waters of the Sierra are also indicative of their sensitivity to inputs of acid deposition. The lake chemistries of dilute

surface waters of sensitive or already acidified lakes in other regions are similar to those for lakes in the Sierra (Melack et al. 1985). Schnoor and Stumm (1985) reported that small lakes in the alpine regions of southern Switzerland are at risk to further inputs of acid deposition due to the thin soils, exposed bedrock, and lack of vegetation in their watersheds and the short residence times of such lakes. The Sierra Nevada watersheds share these characteristics.

The surface waters of the Sierra have low ionic strength and low conductivities (Melack et al. 1985). These characteristics are commonly associated with lakes which are sensitive to acid deposition due to their inability to buffer acid inputs.

Beyond the geological characteristics which make its watersheds sensitive to acid inputs is the fact that the Sierra Nevada receive a large amount of precipitation. Ninety percent of this falls as snow in the alpine zone (Dozier et al. 1987). The pollutants brought in by snow are concentrated as the snow melts in the spring causing a pulse of acidity that is input to surface waters (Dozier et al. 1987). Small increases of pollutants in the future will be magnified in the snowmelt event due to the concentration effect during snowmelt. Experimental acidification of lake and stream waters has been shown to kill insects and microscopic animals (Melack et al. 1987; Cooper et al. 1988). Thus the food chain in these ecosystems can be disrupted as temporary acidification occurs during the snowmelt event. Temporary acidification during summer thunderstorms has also been reported in an Air Resources Board report (Melack et al. 1987).

Models Used in Regional Studies

Models have been developed in order to study the response of watersheds to inputs of acids. The steady state version of the Trickle-down model has been used to determine the lake resources at risk in the upper midwest (Schnoor et al. 1986b) and eastern (Schnoor et

al. 1986a) portions of the United States. This model has also been used as a time-variable

descriptor of the responses of lakes in northeastern Minnesota (Schnoor et al. 1984) and a

stream watershed in Virginia (Muller 1989). The model is based on a mass balance for

alkalinity that studies the transport of acidic material through various compartments in the

watershed.

Henriksen (1979) developed an empirical model based on the theory that the

acidification of a lake can be thought of as a large-scale titration. Melack et al. (1985) used

this model to explain the present chemical condition of 73 lakes sampled in the Sierra

Nevada. It can also be used as a predictor of the condition of lakes under various acid

loadings as will be shown in this study.

This model was developed from water chemistry data for 719 lakes in southern

Norway. The basis of this model is the relationship between lake sulfate concentration,

assumed to be the major anion associated with acid inputs, and the sum of the lake

concentrations of calcium and magnesium, considered to be the major buffering cations

produced by the chemical weathering of minerals. Empirical lines drawn on a plot of the

sum of calcium and magnesium versus excess sulfate in the lake represent the dividing lines

between non-acidified lakes, "transition" lakes, and acidified lakes. Transition lakes are

those that are sensitive to increased acid inputs (Figure 2). In his comparison of

Norwegian models for surface water chemistry, Wright (1984) states that this model is

simply an ionic balance of lake chemistry where all ions other than calcium, magnesium

and sulfate cancel each other out or are in such insignificant concentrations that they can be

neglected.

The major assumption, and perhaps drawback, in this model is that the only source of

acid to the watershed is from inputs of sulfuric acid. This could be a problem with lakes in

California where nitrate can represent a large proportion of anions in deposition (Melack et al. 1985).

Wright and Henriksen (1983) developed a factor, F, which is defined as the change in base cation concentrations in lakewater due to a change in acid anion concentration in lakewater. This is shown in Equation 4

$$F = \frac{\Delta[Ca^{2+} + Mg^{2+}]}{\Delta[SO_4^{2-}]} \qquad (4)$$

This factor will vary depending on the characteristics of the individual lake and the surrounding geology. By varying the change in the concentration of sulfate, one can determine how a lake will respond as far as its ability to compensate for changes in acid loadings through mineral weathering and ion exchange. The lower the value of F, the more sensitive a lake will be to acid loadings since a lesser amount of base cations will be produced for a given increase in acid. A well-buffered lake would have an F-factor of 1.0, while an acidic lake that can no longer buffer inputs of acid would have an F-factor of 0.0.

The acidity of rivers in Newfoundland and Nova Scotia has been studied by Thompson (1982). A cation denudation rate, or the rate at which cations produced from mineral weathering in response to inputs of acid are transported by runoff, was used taking into account all the base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+). This model is basically the same as Henriksen's but essentially assumes what is equivalent to an F-factor of zero. Thus the assumption is that the soils in the watershed are lacking base cations needed for ion exchange. This is due to highly-resistant rock which produces very little or no cations in the weathering process. The results for Thompson's model will be presented in the form of Henriksen's nomograph.
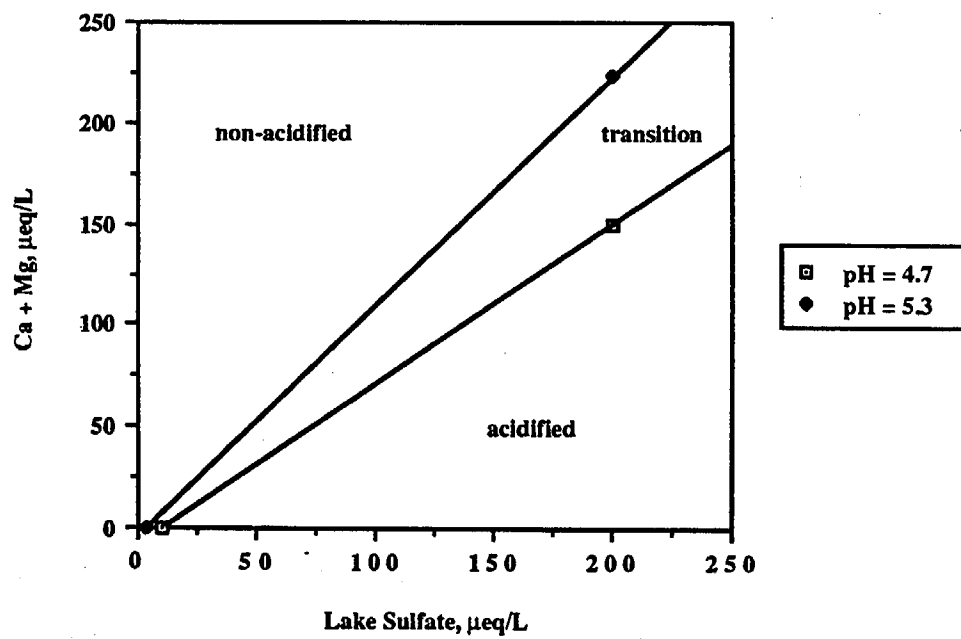
Figure 2. Henriksen's predictor nomograph.

CHAPTER III

METHODS AND ASSUMPTIONS

Database Development

The geographical area considered in this study is the Sierra Nevada in California. The database utilized for this research consists of data from three separate lake surveys: the EPA Western Lake Survey (Landers et al. 1987), data published by Melack et al. (1985), and the California Department Fish and Game survey (1986). The database is henceforth referred to as the University of Iowa (UI) Database. Lake location data in each of the surveys were evaluated and only those in the study area were retained. Duplicate lakes and surface waters which are not technically considered to be lakes (e.g. farm ponds and reservoirs) were omitted (Tonnessen 1988). The number of lakes taken from each survey is shown in Table 2. Figure 3 shows the location of the UI database lakes along with the precipitation monitoring stations managed by the California Air Resources Board. Lake names and coordinate locations for all lakes in the UI database are given in Appendix A.

The U.S. Environmental Protection Agency developed the National Surface Water Survey in an effort to determine the number, location, and characteristics of lakes with little or no acid neutralizing capacity in the United States. The Western Lake Survey (Landers et al. 1987) was conducted, in cooperation with the USDA-Forest Service, in the fall of 1985 and is the sister survey to the previously conducted Eastern Lake Survey (Linthurst et al. 1986). The primary objectives of the Western Lake Survey (WLS) were to determine the percentage and number of lakes with low acid neutralizing capacity (ANC), or alkalinity, the percentage and number of lakes that are acidic, and to provide chemical characteristics of the survey lakes for future studies. A total of 719 lakes in ten western states were

Table 2. The breakdown of the number of lakes that comprise the UI database by lake survey·

Survey	Total number of lakes in survey	Number of lakes in UI database
Western Lake Survey -- Phase I, U.S. Environmental Protection Agency (Landers et al. 1987)	719	102
Statewide Survey of Aquatic Eco-system Chemistry; 1986 (McCle-neghan et al. 1987)	50	28
Major Ion Chemistry and Sensitivity to Acid Precipitation of Sierra Nevada Lakes (Melack et al. 1985)	73	68
Total number of lakes in the UI database		198
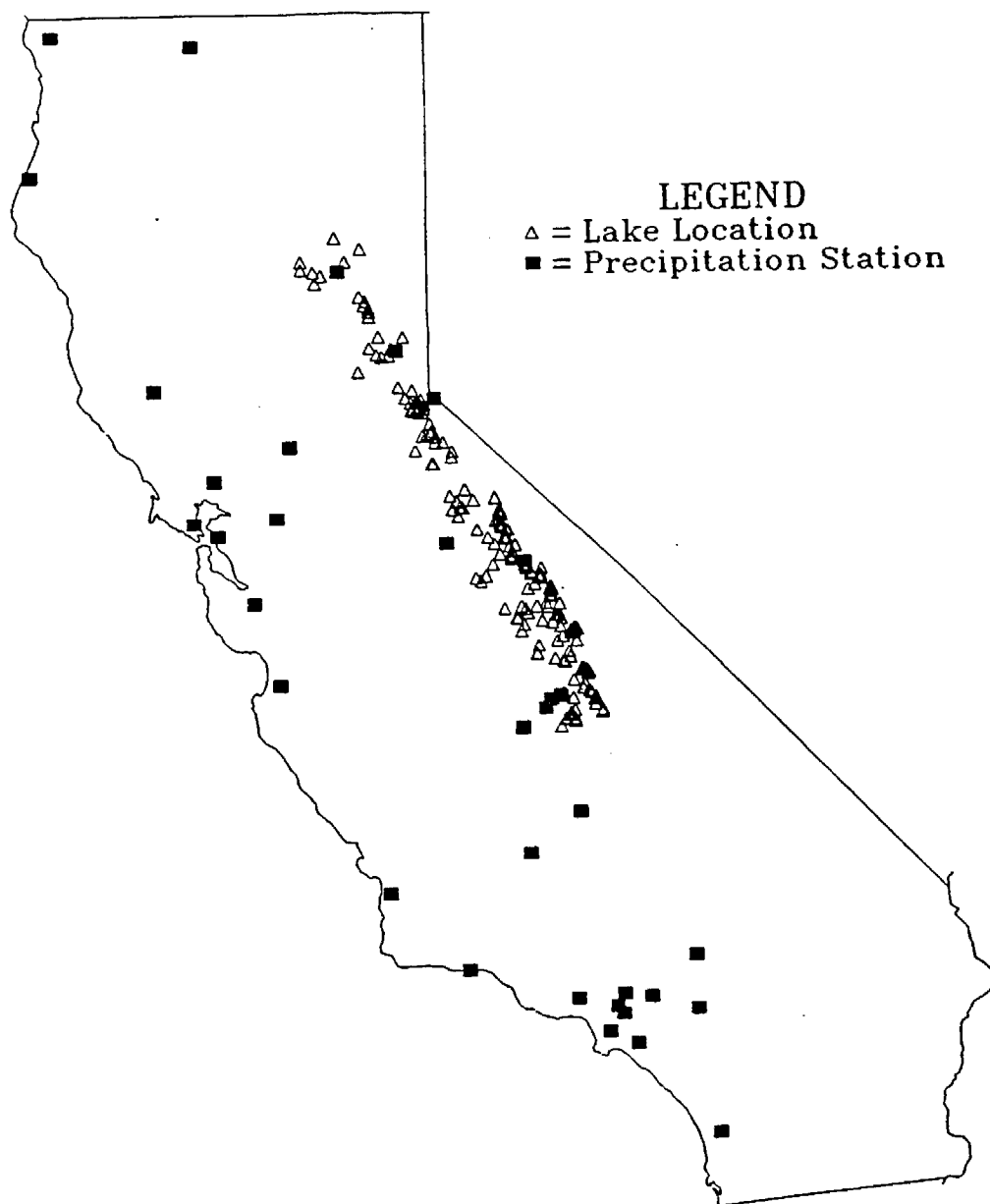
Figure 3. Location of UI database lakes and the precipitation monitoring
stations managed by the Air Resources Board

sampled for numerous physical, geographical and chemical parameters. This represents the most detailed and complete set of data available for lakes in the Sierra Nevada. The largest number of lakes (102) which comprise the the UI database is taken from this survey.

Lakes in the WLS survey were selected by following certain criteria: (1) identifying relatively homogeneous geographic areas within the west; (2) on the basis of historical alkalinity and physiography; and (3) systematically selecting lakes in order to generate a random sample. Three ANC classes (ANC <100, 100-200, and 200-400 μeq/L), or strata, were evaluated in each of of five chosen subregions covering the ten western states. Approximately fifty lakes were then systematically chosen at random within each stratum in order to obtain a true probability sample. Thus chemical characteristics for all lakes within the same subregion could be estimated with known confidence bounds. Acid neutralizing capacity was measured in an analytical laboratory using acidimetric titration and modified Gran analysis (Kanciruk 1987). The California subregion showed the highest percentage (36.7%) of low ANC lakes (ANC $\leq$ 50 μeq/L) versus other subregions in the survey (Eilers et al. 1987a).

The major limitation in the WLS data is that all data are based on a single sample collected in fall 1985. This was done in an effort to minimize within-lake variability. Thus the effect of seasonal variability on the chemical variables in this survey must be considered. However, a separate survey of 50 lakes and streams in California during the fall of 1985 and the spring of 1986 showed no significant difference in ANC and pH between seasons (McCleneghan et al. 1987).

The California Department of Fish and Game, in cooperation with the Air Resources Board, conducted the Statewide Survey of Aquatic Ecosystem Chemistry (McCleneghan et al. 1987). This survey was conducted as part of the Kapiloff Acid Deposition Research and Monitoring Program. The fifty lakes selected for the survey (28 are included in the UI

database) are in areas located in high-elevation areas of the Sierra and other mountainous regions of California. Sampling of the lakes took place during the spring and summers of 1985 and 1986. In addition, the survey was conducted to study the seasonal variability of water chemistry variables and to provide a database for comparison to future studies.

The final survey was conducted by the Department of Biological Sciences at the University of California, Santa Barbara (Melack et al. 1985). Samples were taken from a total of 73 lakes during the summers of 1981 and 1982. ANC was measured in unfiltered water within eight hours of sampling by the Gran titration procedure. This study was an initial attempt to determine the chemical condition of Sierra lakes and to evaluate their sensitivity to increased loadings of acid deposition. A follow-up study was conducted in the spring and fall of 1985 and the results were published in two reports (Melack and Setaro 1986 and Holmes 1986). The acidity levels in the latter study are similar to those reported in the initial study, which indicates that each lake may be considered a steady state system. A total of 68 of these lakes are included in the UI database.

Figure 4 shows the lake chemistries for two of the database lakes. The major cation in the lakes is calcium while the major anion is typically bicarbonate. There are no lakes in the UI database which are currently acidic (ANC ≤ 0). The median concentration values (in $\mu eq/L$) for each ion in all 198 lakes are as follows: Ca^{2+}, 91; Mg^{2+}, 18; Na^+, 28; K^+, 9; HCO_3^-, 112; Cl^-, 7; SO_4^{2-}, 26; and NO_3^-, 1.6.

The lakes in the Melack and Fish and Game surveys were not randomly selected as were the lakes in the Western Lake Survey. Therefore any results obtained from the manipulation of data in the UI database cannot be confidently assumed to represent all lakes in the Sierra Nevada. However, due to the size of the UI database, the conclusions drawn from its use should indicate the general trend among lakes in the study region.

NO3   Cl
      SO4   HCO3

SiO2 = 20 μmol/l

Anions   Σanions = 45

H
      Ca   Mg   K   Na

Cations   Σcations = 50

                                          pH = 6.3

0   1 0   2 0   3 0   4 0   5 0   6 0

Concentration, μeq/l

Emerald Lake

NO3   SO4   SiO2 = 14.0 μmol/l
      Cl   HCO3

Anions   Σanions = 58.9

H   NH4
      Ca   Mg   K   Na

Cations   Σcations = 65.8

                                          pH = 6.80

0   1 0   2 0   3 0   4 0   5 0   6 0   7 0

Concentration, μeq/l

Goose Lake
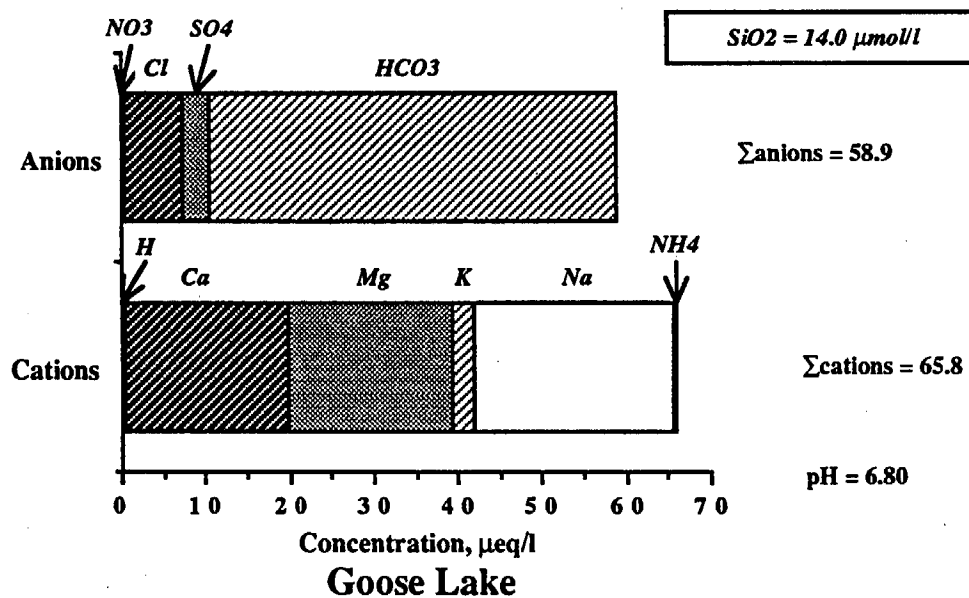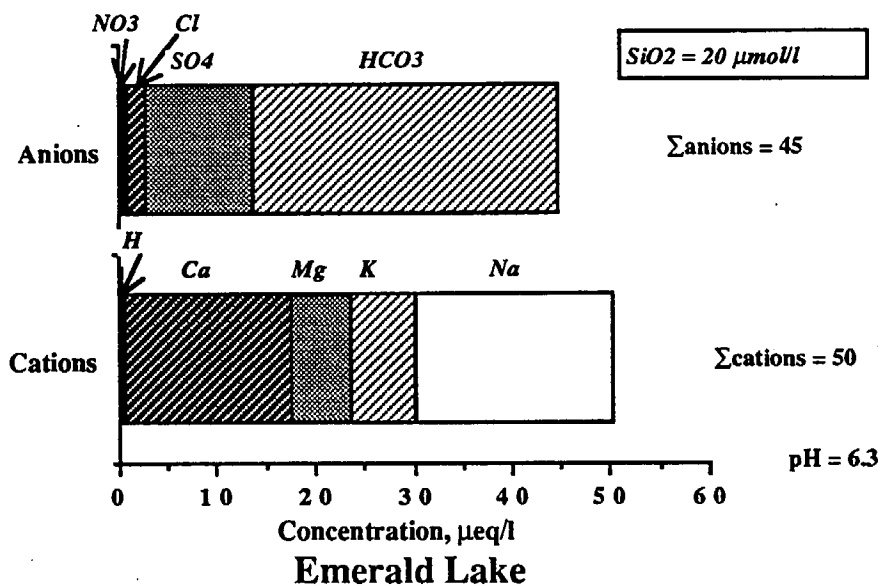
Figure 4. Typical lake chemistries for two lakes in the UI database.

Deposition Chemistry and Annual Rates

Wet precipitation chemistry was assigned for each lake based on proximity to one of seven wet deposition stations operated by the California Air Resources Board (CARB 1988a and 1988b). The seven deposition monitoring stations and their locations are listed in Table 3. The data used were volume-weighted mean concentrations of solutes in wet deposition for the period 1984-1987.

Figure 5 shows the monthly variability of hydrogen ion concentration at Giant Forest in Sequoia National Park (Stohlgren and Parsons, 1987). The peak H^+ concentrations are recorded in the summer months when less precipitation volume is measured.

Dry deposition chemistry was available for Emerald Lake in Sequoia National Park in the southern Sierra. Detailed dry deposition chemistry was collected by Bytnerowicz and Olszyk (1988). The ion concentrations reported were from needle washings of lodgepole and western white pines. The concentrations used are shown in Table 4. The data were extrapolated based on a four-month summer exposure period as this is when most dry deposition occurs. The dry deposition amounts are also based on the normal annual precipitation (111 cm/yr) which falls at Emerald Lake. These data were originally reported in ranges of deposition fluxes for each ion. In order to maintain a balance in the ion budget for total deposition chemistry, the larger values for the anions and the smaller values for the cations were used. Dry deposition ion concentrations for all species were then added to wet chemistry values to obtain a total deposition chemistry. Wet deposition amounts were greater than dry amounts. Table 5 shows the deposition fluxes for sulfate and nitrate at Emerald Lake. Figure 6 shows a bar diagram for the total deposition chemistry at the Emerald Lake precipitation station.

Cahill et al. (1986) conducted regional studies which showed that Sequoia National Park is representative of large areas of the western slope of the Sierra in the flux of dry

Table 3.   The location of the seven wet deposition monitoring stations in California that provide the precipitation chemistry.

Name	Latitude	Longitude	Elevation (m)
Mammoth	37°38'30"	119°02'15"	2926
Quincy	39°57'55"	120°58'00"	1061
Sequoia			
Emerald Lake	36°35'50"	118°40'30"	2800
Giant Forest	36°34'09"	118°46'40"	1890
Soda Springs	39°19'30"	120°22'00"	2063
South Lake Tahoe	38°56'45"	119°58'00"	1900
Yosemite	37°47'40"	119°51'20"	1395
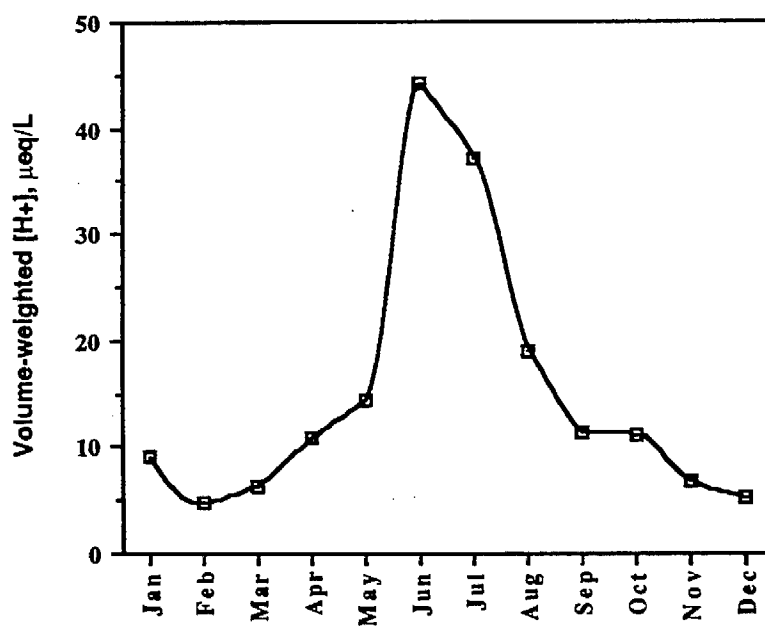
Figure 5.   Monthly variability of volume-weighted hydrogen ion
concentration in wet deposition at Giant Forest (Stohlgren and
Parsons, 1987).

Table 4. Dry deposition values reported by Bytnerowicz and Olszyk (1988) from Lodgepole and Western White Pines in Sequoia National Park.

Ion	Deposition Flux ($\mu eq/m^2 \cdot hr$)	Concentration* ($\mu eq/L$)
NO_3^-	0.597	1.55
SO_4^{2-}	0.121	0.31
Cl^-	0.383	1.00
PO_4^{3-}	0.067	0.17
F^-	0.066	0.17
NH_4^+	0.163	0.42
Ca^{2+}	0.300	0.78
Mg^{2+}	0.216	0.56
Na^+	0.564	1.47
H^+	0	0

* Concentration is estimated in this report as the dry deposition flux divided by the annual precipitation (in meters). This is equivalent to dissolving the total dry deposition flux into the volume of precipitation water.

Table 5. Deposition fluxes of the major acid anions at Emerald Lake and in the Eastern United States.

	Wet		Dry		Total	
	$\frac{kg}{ha\text{-}yr}$	$\frac{eq}{ha\text{-}yr}$	$\frac{kg}{ha\text{-}yr}$	$\frac{eq}{ha\text{-}yr}$	$\frac{kg}{ha\text{-}yr}$	$\frac{eq}{ha\text{-}yr}$
Emerald Lake, California[*]						
SO_4^{2-}	3.13	65.17	0.17	3.44	3.30	68.61
NO_3^-	12.42	200.29	1.07	17.18	13.49	217.47
NH_4^+	5.10	283.45	0.08	4.65	5.18	288.10
Eastern United States[†]						
SO_4^{2-}	33.60	700.00	12.48	260.00	46.08	960.00
NO_3^-	12.40	200.00	5.21	84.00	17.61	284.00
NH_4^+	2.16	120.00	0.79	44.00	2.95	164.00

[*]California Air Resources Board and Bytnerowicz and Olszyk 1988.
[†]Lindberg et al. 1986.
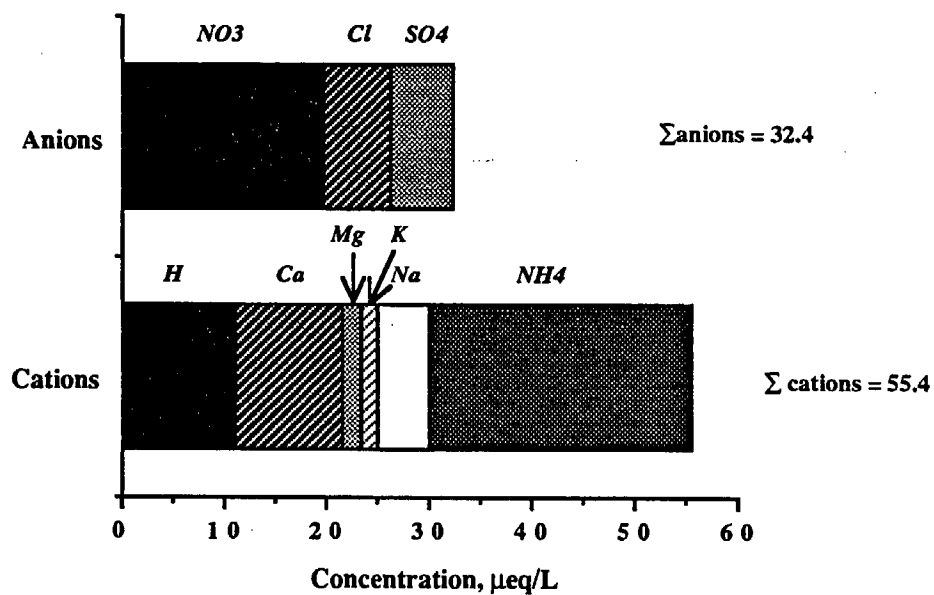
Figure 6. Total deposition (wet plus dry) chemistry for the Emerald
Lake precipitation station. Wet deposition chemistry data
based on volume-weighted mean ion concentrations for the
period 1984-1987. Dry deposition chemistry taken from needle
washings of pine trees at Emerald Lake in 1987.

deposition in summer. Assuming that dry deposition values at Emerald Lake are typical throughout the Sierra, on the average for all precipitation stations used, dry deposition of sulfate was 6% of the wet deposition concentration accounting for 6% of the total deposition sulfate. Dry deposition of nitrate, on the other hand, was found to be 23% of wet deposition and accounted for 20% of the total deposition nitrate indicating that dry deposition plays a major role in the transport of nitrate to environmental systems. Dry deposition of ammonium was found to be 5% of the wet deposition and 5% of the total deposition.

The amount of wet deposition at each lake was determined from maps of yearly and percent normal precipitation (Department of Water Resources 1985). Lake locations were plotted on a map of California. Transparencies of the precipitation maps were placed over the lake location maps and an annual precipitation value and a percent normal precipitation value was estimated for each lake. The normal (based on data for the period 1931-1980) annual precipitation rates could then be calculated. Total deposition chemistries are given in Appendix C.

Assumption of an Evapoconcentration Factor

The evapoconcentration factor is a major assumption used in this model. Evapoconcentration factors for all the lakes were calculated based on the ratio of the sulfate concentration in the lake to the total current sulfate concentration in current deposition as given in Equations 5 and 6.

$$[SO_4^{2-}]_{lake} = E[SO_4^{2-}]_{precip} \tag{5}$$

$$E = \frac{[SO_4^{2-}]_{lake}}{[SO_4^{2-}]_{precip}} \tag{6}$$

The assumption here is that there are no other external or internal sources of sulfate in the watershed. This is a valid assumption as the majority of net sulfate reactions in the watersheds as given by Equation 10 are between -5 and 5 μeq/L as will be shown later (see Figure 12). All values of E less than 1.0 and greater than 3.5 were disregarded as unreasonable and an average of 2.0 was calculated (83 or 42% of the lakes fell within this range).

Based on the large number of data points available from the EPA Western Lake Survey, which contributes a majority of the lakes in the UI database, the evapoconcentration factor was calculated for each of the WLS lakes using the assigned annual precipitation amount (I) and the annual surface water runoff (Q). The evapoconcentration factor is the ratio of I/Q. It was considered that this would be a more accurate method of calculating E. Lakes which had values that were not between 1.0 and 3.5 were assigned the average value of 2.0 as calculated using the lake and deposition sulfate concentrations. The 96 lakes not included in the WLS were assigned the average value of 2.0, again based on the ratio of sulfate concentration in the lake and in total deposition. The calculated evapoconcentration factor for each lake is given in Appendix C.

Lee and Schnoor (1988) Reactions Model

Lee and Schnoor (1988) used a simple mass balance equation to determine the reactions which take place in lake watersheds in the Adirondack Mountains, the Southern Blue Ridge Province of the Appalachian Mountains, and a portion of northern Florida. The reactions for major ions in the watersheds of lakes in the Sierra were determined using this model. This model was further developed in order to calculate the individual reaction rates and removal fractions for sulfate, nitrate and ammonium in the watershed of each lake.

A check on the ion budgets for the lakes in the UI database was also performed. The average total error (taking the absolute value of the percent error) and the actual average error from this analysis will be presented in the following chapter.

The general mass balance equation around a defined control volume, in this case the watershed, for a particular ionic species can be written as

$$accumulation = inputs - outputs \pm reactions \qquad (7)$$

where the negative (-) sign on the reactions term indicates a decrease or consumption of the ion and a positive (+) sign indicates an increase or production of the ion. All reactions in the watershed in this model are assumed to be first-order. The concentration of the ion remains constant with time under steady state conditions. After rearrangement this reduces Equation 7 to

$$\pm reactions = outputs - inputs \qquad (8)$$

or for a watershed that contains a lake discharge to

$$\pm reactions = QC_{lake} - IC_{precip} \qquad (9)$$

where Q=annual surface water runoff (L/yr), I=annual precipitation (L/yr), C_{lake}=ion concentration in the lake (µeq/L), and C_{precip}=ion concentration of precipitation (µeq/L). Dividing Equation 9 by the annual runoff gives

$$RXN = \frac{reactions}{Q} = C_{lake} - EC_{precip} \qquad (10)$$

where E=I/Q=evapoconcentration factor, which takes into account water losses due to evaporation, and RXN=net reaction for a particular ion (μeq/L). The major assumption here is that all outflow from the watershed goes through the lake; hydrologically, it is assumed to be a "tight" system. Thus, groundwater inflows and outflows to and from the watershed are assumed negligible. As stated before, a positive RXN term would indicate a production of the ion by some process or processes in the watershed and a negative RXN term a consumption of the ion. A RXN term close to zero would indicate a conservative ion with little or no reaction in the watershed. It should be noted that when calculating the RXN term for ANC, the precipitation concentration used will be that of hydrogen ion. Hydrogen ion is taken as the negative value of alkalinity (acid neutralizing capacity) and will thus change the sign preceding the C_{precip} term in Equation 10.

Development of Equations to Calculate Removal Fractions

Sulfate, nitrate and ammonium are consumed by biological reactions which take place in the watershed. The more common reactions are given in Table 6. The reaction rates of each ionic species can be calculated and then used to check the quality of the hydrologic variables used in this analysis by noting the fit of the data relative to a theoretical line describing the first-order decay of an ion in a steady state, completely mixed, flow-through system. Assuming first-order reactions, Equation 9 becomes

$$-kC_{lake}V_{lake} = QC_{lake} - IC_{precip} \qquad (11)$$

where k is the first-order reaction rate (yr^{-1}), in this case, for the consumption of an ion (nitrate, sulfate, or ammonium) in the watershed, and V_{lake} is the volume of the lake in liters. According to Equation 10 the right side of Equation 11 is the reactions term and so

Table 6. Biological reactions which consume sulfate, nitrate and ammonium in lake
watersheds (Lin et al. 1986).

Sulfate reactions:

Biological reduction $\quad\quad SO_4^{2-} + 2CH_2O \text{ -------> } H_2S + 2HCO_3^-$

$$OH^- \quad OH^-$$

Ion exchange/sorption $\quad\quad SO_4^{2-} + R \text{ ------------> } R\text{-}SO_4 + 2OH^-$

Nitrate reactions:

Denitrification $\quad\quad 5CH_2O + 4NO_3^- + 4H^+ \text{ -------> } 5CO_2 + 2N_2 + 7H_2O$

Nitrate $\quad\quad\quad\quad NO_3^- + 5CO_2 + 4H_2O \text{ --------> } C_5H_7NO_2 + 7O_2 + OH^-$
Assimilation

Ammonium reactions:

Nitrification $\quad\quad\quad\quad NH_4^+ + 2O_2 \text{ --------> } NO_3^- + H_2O + 2H^+$

Ammonium $\quad\quad\quad NH_4^+ + 4CO_2 + HCO_3^- + H_2O \text{ -----> } C_5H_7NO_2 + 5O_2$
Assimilation
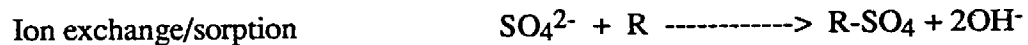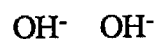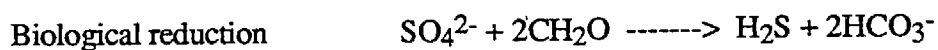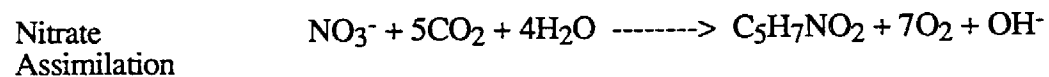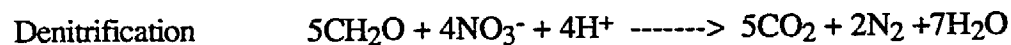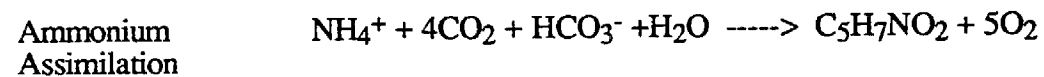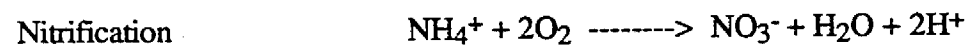
$$-kC_{lake}V_{lake} = Q*RXN \qquad (12)$$

Therefore the reaction rate constant can be calculated by

$$k = \frac{-Q*RXN}{C_{lake}V_{lake}} \qquad (13)$$

where Q can be calculated using the evapoconcentration factor (E = I/Q). The RXN term in this case would be for current deposition loadings.

Writing out Equation 7 for the general case with first-order reactions over a period of time, t, gives

$$V_{lake}\frac{dc}{dt} = Q_{in}C_{precip} - Q_{out}C_{lake} - kC_{lake}V_{lake} \qquad (14)$$

where $Q_{in} = I$, where I is the annual precipitation (L/yr), and $Q_{out} = Q$, the annual surface water runoff (L/yr). Dividing by the lake volume and realizing that $Q_{in} = EQ_{out}$ and that the residence time, τ, of a lake is equal to V_{lake}/Q_{out}, Equation 14, assuming steady state, becomes

$$0 = \frac{E}{\tau}C_{precip} - \frac{1}{\tau}C_{lake} - kC_{lake} \qquad (15)$$

Rearranging gives

$$\frac{C_{lake}}{EC_{precip}} = \frac{1}{1 + k\tau} \qquad (16)$$

which is similar to the steady state condition for a completely-mixed, flow-through system except that the evapoconcentration factor is taken into account here. The removal fractions for the reactive ions, sulfate, nitrate and ammonium, can be evaluated by plotting C_{lake}/EC_{precip} versus $k\tau$. The ordinate value for each lake is the fraction remaining in the lake at steady state. Subtracting this value from one gives the fraction of the ion that has been consumed once steady state conditions have been reached. These values will be used in the analysis of changes in ammonium nitrate in deposition as applied to the steady state charge balance model to be discussed later. It should be noted that sufficient data for this analysis were only available for the 102 lakes taken from the EPA Western Lake Survey.

Henriksen and Thompson Models

Watershed mineralogy determines the extent of chemical weathering that takes place in response to inputs of acid. Detailed geologic data for each lake are unavailable. As stated earlier, granitic bedrock, which does not weather rapidly, is characteristic of most of the Sierra Nevada. Therefore changes in lake sulfate were analyzed by using F-factors of 0.2, 0.4 and 0.6 when applying the database to Henriksen's nomograph. This is also a reasonable assumption as very little ion exchange is likely to occur due to the thin soils characteristic of the Sierra Nevada.

Changes in the amount of lake sulfate can give an indication of how lakes will react to different acid deposition loadings. Recall that Henriksen's nomograph assumes that sulfate is the major anion associated with acid. Loadings of twice (+100%) and half (-50%) the existing lake sulfate were used in this analysis. Changes in the major base cations (calcium and magnesium) were calculated according to the particular F-factor. The resulting new lake concentrations were plotted on the nomograph and percentages of

sensitive and acid lakes could then be determined. These two loading scenarios were applied to both Henriksen's (F = 0.2, 0.4 and 0.6) and Thompson's (F = 0.0) models.

Steady State Charge Balance Model

The acid neutralizing capacity in a lake can be determined by a charge balance as shown in the following equations:

$$\sum[\text{Base cations}] = \sum[\text{Acid anions}] \qquad (17)$$

$$[\text{ANC}] = \sum[\text{Base cations}] - \sum[\text{Acid anions}] \qquad (18)$$

$$[\text{ANC}] = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] +$$
$$[NH_4^+] - [SO_4^{2-}] - [NO_3^-] - [Cl^-] \qquad (19)$$

where [ANC] is taken to be the bicarbonate concentration, $[HCO_3^-]$, and all concentrations are in $\mu eq/L$. The change in the concentration of acid neutralizing capacity due to changes in deposition loadings can also be determined in a similar manner

$$\Delta[\text{ANC}] = \Delta\sum[\text{Base cations}] - \Delta\sum[\text{Acid anions}] \qquad (20)$$

Note that $\Delta\sum[\text{Acid anions}]$ term in Equation 20 excludes bicarbonate ion as shown in Equation 19.

This is the basis for the steady state charge balance model. The development of the model for different loading scenarios will be shown after a brief discussion of the assumptions made and the loading scenarios used in this analysis. It should be kept in

mind that the changes in the lake ANC will be the final value reached once sufficient reaction time in the watershed has elapsed. This is usually on the order of one hydraulic retention time. This is the definition of a steady state system.

Assumptions

The steady state charge balance model does not consider the potential for episodic acidification during snowmelt and summer storm events. It uses annual average precipitation chemistry and summer or fall index lake chemistry to assess the potential for chronic acidification.

A Henriksen F-factor, or cation replenishment rate (Δcations/Δsulfate), of 0.4 was also assumed. This indicates that increases in acid deposition are only partially compensated by the release of base cations due to chemical weathering. As stated earlier, an F-factor of 1.0 would indicate a perfectly buffered system, able to neutralize any and all acid inputs. An F-factor of 0.4 means that 40% of the increase in acid will be neutralized and result in the release of an equivalent amount of base cations into the watershed.

Deposition Loading Scenarios

Three sets of acid loading scenarios were used as chosen by the California Air Resources Board (Tonnessen 1988). It should be noted that the term "loading" used in this research refers to ion concentrations of deposition and not mass quantities of chemical substances. A factor analysis was performed by CARB on precipitation data collected at Emerald Lake and Giant Forest in Sequoia National Park. This analysis concluded that the strongest association of ions in precipitation was between H^+ and SO_4^{2-} and NO_3^- and NH_4^+.

The first scenario assumed that sulfuric acid, H_2SO_4, would be the dominant contributor of acid to the watershed. This is not strictly true as there is a significant amount of organic acids in precipitation. Levels of nitric acid may be significant but these data need additional analysis before a conclusion can be reached. This was assumed to hold true for both wet and dry deposition. The change in the amount of acid (H^+) in deposition was taken to be equal to the change in the amount of sulfate in deposition.

The second scenario assumed ammonium nitrate (NH_4NO_3) as the dominant acid contributor through deposition onto the watershed. While there is no direct change in the acid contributed by deposition to the watershed in this scenario, ammonium and nitrate undergo biological reactions which affect the ANC in the lake. These reactions were given in Table 6. The change in loading was based on deposition of ammonium as it is in smaller quantities in deposition than is nitrate. An equivalent amount equal to the change in deposition ammonium was also added to the nitrate in deposition. This corresponds to $NH_4^+/NO_3^- = 1.0$. The case for $NH_4^+/NO_3^- = 1.5$ was also studied.

The final scenario studied was a combination of both sulfuric acid and ammonium nitrate. The changes in loadings were as previously described and were taken to be additive in their effect on the ANC in the watershed. The same two changes in deposition loadings as used for the Henriksen nomographs (+100% and -50%) were employed for the charge balance model.

Each scenario was also analyzed for the case of a wet and a dry precipitation year. The charge balance model is affected in this analysis by the amount of dry deposition and the evapoconcentration factor. Dry deposition amounts are dependent on the amount of wet deposition as this is the major mode of transport by which these ions are carried from trees and soil to the lake. The Air Resources Board recommended using precipitation amounts of 3.0 m/yr for a wet season and 1.0 m/yr for a dry season. Since dry deposition

concentrations used have been based on the normal annual precipitation at Emerald Lake (1.11 m/yr) it will be assumed that a dry year will correspond to 0.8 m/yr wet precipitation.

The evapoconcentration factor is dependent on the climatological conditions which exist at the lake. More evaporation will take place in warmer climates, and conversely, less water will be lost through evaporation in cooler periods. It is assumed that the evapoconcentration factor in a dry year will be 2.5 and in a wet year will be 1.5.

The scenarios used were assumed for two reasons: (1) most previous studies in the midwest and northeastern United States and Canada considered only changes in sulfuric acid deposition; and (2) the situation in some parts of California is such that the proportion of nitrate contributing to acid deposition may be greater than that found in other parts of the United States (Tonnessen 1988; Ashbaugh et al. 1988). It is believed that nitrate loadings in the form of ammonium nitrate are more prevalent than those in the form of nitric acid in the southern Sierra on the Western slope (Tonnessen 1988). Should sources fo NH_3 in the Central Valley be reduced, this relationship will undoubtedly change.

Model Development

The first scenario analyzes the effect on lake ANC due to changes in sulfuric acid loadings only. In this case the change in cations is due to the change in base cation concentration caused by chemical weathering and ion exchange in the watershed. This is given by the Henriksen F-factor. The change in strong acid anions in Equation 20 is only affected by the change in sulfate of precipitation. The change in ANC in the lake is simply

$$\Delta[ANC] = \Delta[\text{Base cations}]_{lake} - \Delta[SO_4^{2-}]_{lake} \qquad (21)$$

$$\Delta[ANC] = 0.4 \, (E)(\Delta[SO_4^{2-}]_{precip}) - (E)(\Delta[SO_4^{2-}]_{precip}) \qquad (22)$$

$$\Delta[ANC] = -0.6 \, (E)(\Delta[SO_4^{2-}]_{precip}) \qquad (23)$$

This makes sense as an increase in deposition loading would mean a positive $\Delta[SO_4^{2-}]_{precip}$ term and thus a negative change in ANC concentration in the lake as shown in Equation 23. Conversely, a decrease in deposition loading would yield a negative change in deposition sulfate and thus a positive change in lake ANC. The new ANC concentration in the lake is given by Equation 24,

$$[ANC] = [ANC]_0 + \Delta[ANC] \qquad (24)$$

where $[ANC]_0$ is the current acid neutralizing capacity (as calculated by Gran alkalinity titration) prior to changes in sulfuric acid deposition. The change in the amount of acid (H^+) was taken to be equal to the change in the amount of sulfate according to dissolution in water.

The second scenario looked at changes in ammonium nitrate of deposition. In this scenario, the change in cations is due to the change in deposition ammonium and the change in anions is due to the change in deposition nitrate. It is assumed that all of the change in deposition of ammonium is nitrified or taken up by plants and algae. Both of these processes have an acidifying effect. Actual nitrate removal fractions for the 102 lakes taken from the Western Lake Survey, as determined from Equation 16, were used to describe the change in deposition of nitrate as it undergoes biological reactions (denitrification or plant uptake) in the watershed. These are alkalizing reactions. The remainder of the lakes were assigned the average nitrate removal for the Western Lake Survey lakes. These are conservative assumptions that are supported by survey data.

Complete (100%) reaction of both nitrate and ammonium would result in no net effect on the lake ANC since they are in roughly equivalent amounts. The validity of these assumptions and the determination of the nitrate removal rates are discussed in the next chapter. The change in lake ANC, then, is

$$\Delta[ANC] = \Delta[NH_4^+]_{lake} - \Delta[NO_3^-]_{lake} \tag{25}$$

But since all of the additional ammonium will undergo biological reactions, Equation 25 reduces to

$$\Delta[ANC] = -\Delta[NO_3^-]_{lake} \tag{26}$$

A certain percentage of the nitrate will undergo biological reactions such that

$$\Delta[ANC] = -((E)(\Delta[NO_3^-]_{precip}) - R(E)(\Delta[NO_3^-]_{precip})) \tag{27}$$

$$\Delta[ANC] = -(1 - R)(E)(\Delta[NO_3^-]_{precip}) \tag{28}$$

where R is the fraction of nitrate removal in the watershed due to biological reactions. The change in loading was based on deposition of ammonium as it is in slightly smaller quantities in deposition than is nitrate. An equivalent amount equal to the change in deposition of ammonium was also added to the nitrate in deposition.

The biological reactions that consume ammonium and nitrate were shown in Table 6. Nutrient deficient soils, such as those found in the Sierra, usually consume ammonium by ammonium assimilation, or plant uptake.

$$NH_4^+ + 4CO_2 + HCO_3^- + H_2O \longrightarrow C_5H_7NO_2 + 5O_2$$
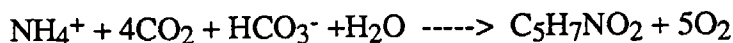
In this case, the model described for changes in ammonium nitrate with a $NH_4^+/NO_3^- = 1:1$ in deposition accurately describes the change in ANC in the lake. This is due to the one-to-one nature of the reaction of ammonium and ANC (HCO_3^-). However, if part of the ammonium in the system is consumed via nitrification,

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$$
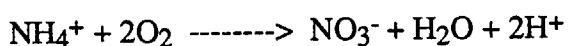
an error is introduced which will reach a maximum value of 1-R if all the ammonium is consumed by this reaction rather than plant uptake. This is due to the fact that for every equivalent of ammonium consumed, two equivalents of acid are produced along with one equivalent of nitrate. There are then two equivalents of nitrate that will be consumed according to the value of R for biological reactions of nitrate. As a result there will be a quantity of nitrate left unreacted equal to 2(1-R). The model assumes that ammonium is entirely consumed by plant uptake. This means that the value of nitrate remaining after biological reactions is 1-R. This is where the error comes into play. The actual pathway taken by ammonium in the watersheds of the Sierra is unknown at this time. The possible error which might arise should ammonium be consumed all or in part by nitrification will be discussed in Chapter IV.

It should be pointed out that changes in ammonium and nitrate in deposition that are not in equal amounts will result in a greater net acidifying or greater net alkalizing effect on lakes. The ratio of NH_4^+/NO_3^- in deposition is an indication of what effect the biological processes will have in the watershed. It is clear that ratios greater than 1.0 will produce an acidifying effect. Since it is of major interest to determine the number of lakes that may

become acid in the future, this study will look at the case of $NH_4^+/NO_3^- = 1.5$ and not consider ratios less than 1.0.

In this case, the change in ANC in the lake will be equal to the amount of acid produced in the complete consumption of ammonium less the amount of ANC produced in the consumption of nitrate.

$$\Delta[ANC] = (E)(\Delta[NH_4^+]_{precip}) - (E)(R)(\Delta[NO_3^-]_{precip}) \qquad (29)$$

$$\Delta[ANC] = (E)(\Delta[NH_4^+]_{precip} - (R)(\Delta[NO_3^-]_{precip})) \qquad (30)$$

The maximum error that would occur in this analysis for consumption of ammonium by nitrification would be equal to a value of the ratio of NH_4^+/NO_3^- multiplied by (1-R)

The third scenario combined changes in deposition loadings for both sulfuric acid and ammonium nitrate. The overall change in ANC is the sum of the changes due to various sulfuric acid and ammonium nitrate loadings as previously derived.

$$\Delta[ANC] = \Delta[ANC]_{SO_4^{2-}} + \Delta[ANC]_{NO_3^-} \qquad (31)$$

where $\Delta[ANC]_{SO_4^{2-}}$ is the change in lake ANC due to changes in sulfuric acid loadings (see Equation 23), and $\Delta[ANC]_{NO_3^-}$ is the change in ANC due to changes in ammonium nitrate loadings (Equation 28). Thus the change in lake ANC for combined changes in sulfuric acid and ammonium nitrate is

$$\Delta[ANC] = [-0.6 \ (E)(\Delta[SO_4^{2-}]_{precip})] + [(1 - R)(E)(\Delta[NO_3^-]_{precip})]. \qquad (32)$$

For the case where the change of ammonium is greater than the change in nitrate, Equation 32 becomes

$$\Delta[ANC] = [-0.6 \ (E)(\Delta[SO_4^{2-}]_{precip})] +$$

$$[(E)(\Delta[NH_4^+]_{precip} - (R)(\Delta[NO_3^-]_{precip}))] \qquad (33)$$

The results of each scenario are plotted as a cumulative proportion of lakes versus predicted ANC. The cumulative proportion of lakes plotted against their present acid neutralizing capacity can give an indication as to how many lakes are currently acidic or highly sensitive to further acid loadings. These plots and the analysis of their results are presented in Chapter IV, Results and Discussion.

CHAPTER IV

RESULTS AND DISCUSSION

Check on Database Quality

Ion budgets were calculated for each lake in the UI database. Due to electroneutrality, the sum of the cations must equal the sum of the anions. This is another measure of the quality of the database in terms of the chemical concentrations given. Summations of the major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^+) and anions (HCO_3^-, SO_4^{2-}, NO_3^-, and Cl^-) were calculated and the percent error determined as follows:

$$\% \text{ error} = \frac{\Sigma[\text{cations}] - \Sigma[\text{anions}]}{\Sigma[\text{cations}]} \times 100 \tag{35}$$

The overall average error in the ion budget was calculated by taking the absolute value of the percent error and then determining the average. This value was found to be $13 \pm 11\%$. The actual error was found by simply taking the average of the actual percent error. This value gives an indication of the bias of the error in the ion budgets. The actual error was calculated as $6 \pm 16\%$. This indicates that the sum of the cations in the watersheds is generally 6% greater than the sum of the anions. This is considered to be in the acceptable range for ion budgets.

Current Condition of UI database Lakes

Database Manipulation

Figure 7 shows the cumulative proportion of lakes in the UI database plotted versus current acid neutralizing capacity. The percentage of lakes with ANC $\leq$ 50 μeq/L in the UI database is 38% (75 out of 198 total lakes). Table 1 showed the results for other studied regions in the United States. While there are no acidic (ANC < 0) lakes in the Sierra, there is a greater percentage of lakes which are sensitive to further inputs of acidic deposition than in any other part of the U.S.

Figure 7 does not indicate if lakes in the Sierra have become more acidic over the years. Melack et al. (1985) stated that the lack of past data makes it impossible to determine if there has been a change in alkalinity over the years. However, as stated earlier, a follow-up study done on lakes sampled by Melack et al. (1985) reported that acidity levels were similar from one year to the next (Melack and Setaro 1986).

Generally there is a one-to-one relationship between acid neutralizing capacity and the sum of the base cations in a lake. Changes in the acid concentration input to the watershed are typically compensated for in a natural buffering system by a release of base cations from the chemical weathering of rocks and minerals in the watershed as shown in the following equation:

$$CaCO_3 + H_2CO_3 \iff 2HCO_3^- + Ca^{2+} \qquad (36)$$
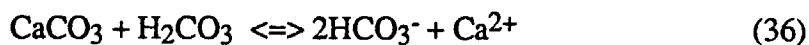
This is the naturally occurring process that is commonly referred to as carbonic acid weathering. As stated earlier, there is an amount of CO_2 present in the atmosphere that is in equilibrium with the lake. This is a natural source of acid to the lake. Figure 8 shows a plot of the sum of the base cations existing in the lakes versus the current acid neutralizing
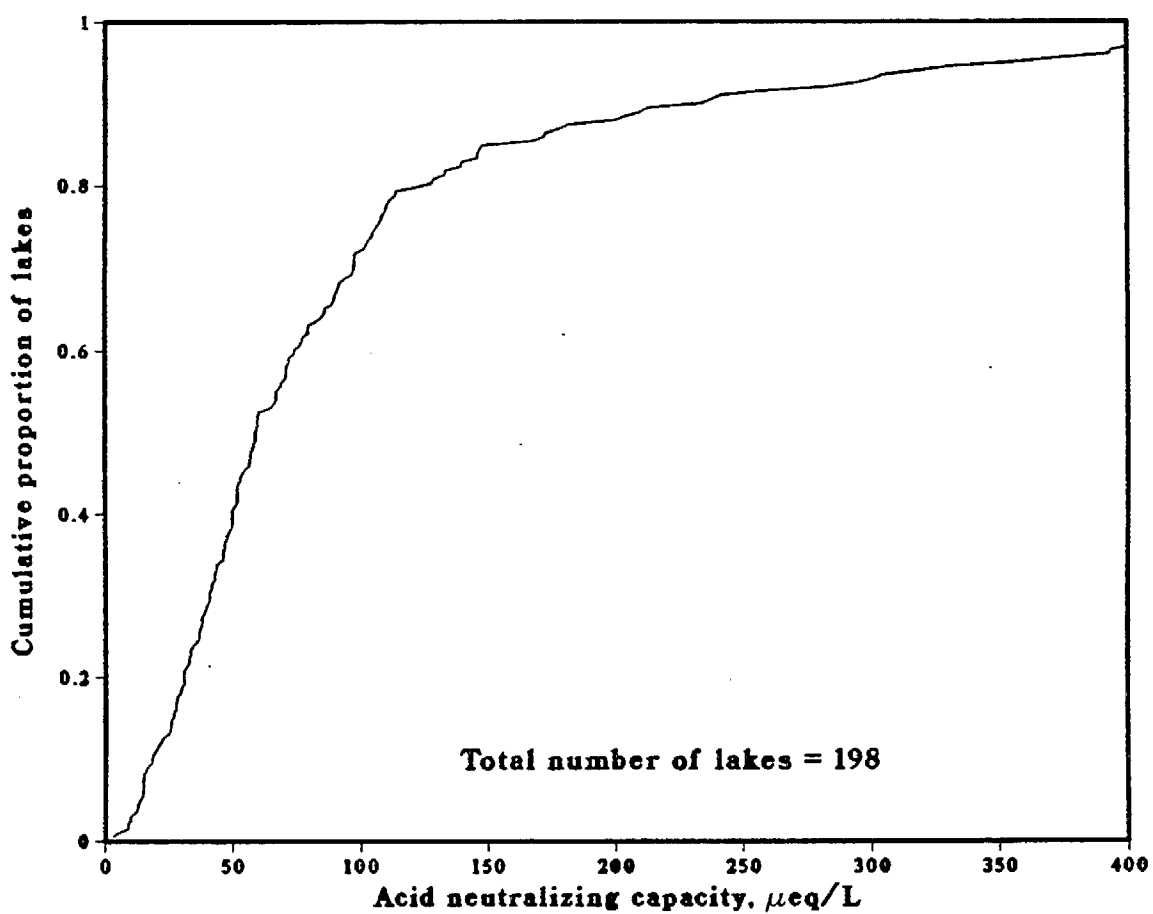
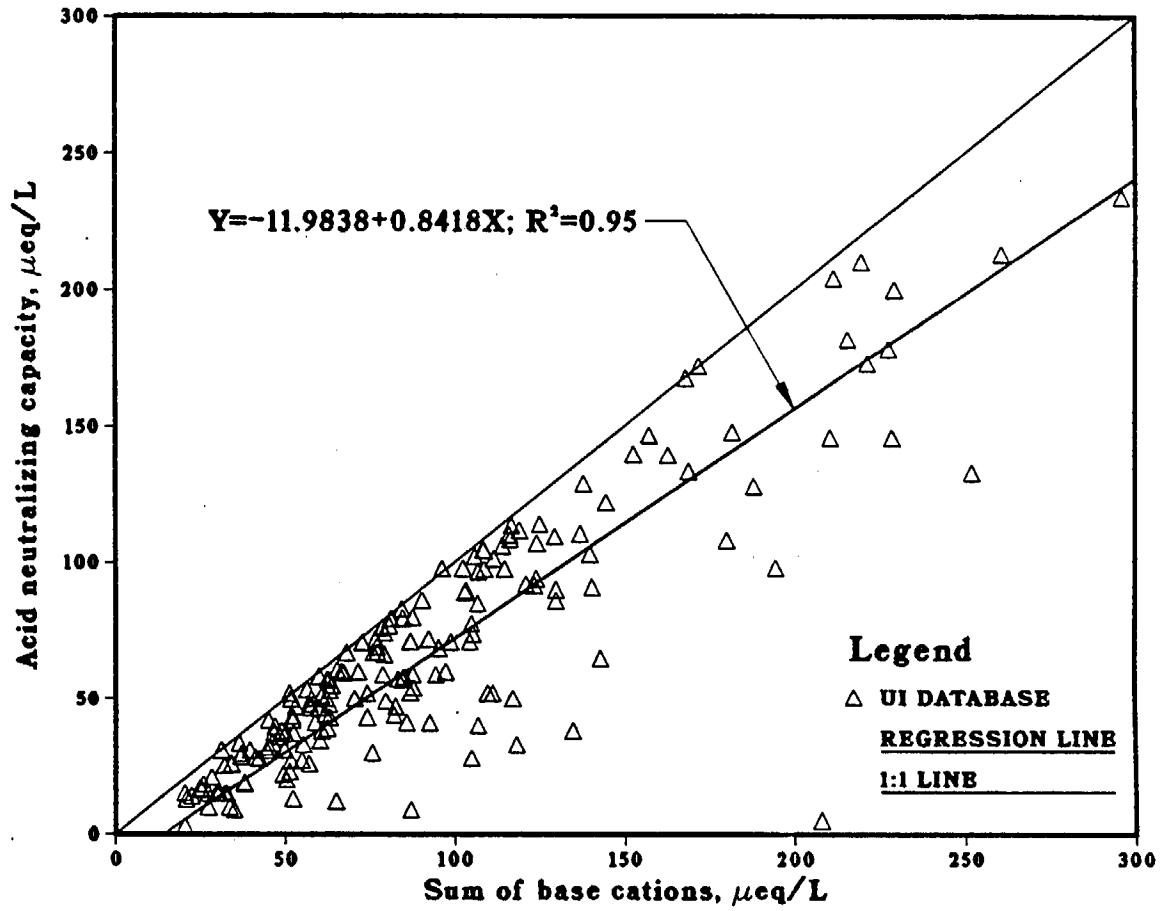Figure 7. Current chemical condition of UI database lakes.

Figure 8. Acid neutralizing capacity versus the sum of the base cations in UI database lakes.

capacity. The curve fit shows a nearly linear relationship (slope = 0.8418 with an R^2 = 0.95). The majority of the data, however, do seem to follow a one-to-one relationship (the upper limit of the scatter) with a few lakes straying below the this line. The reason for the variance of these lakes from the expected relationship may be due to biological redox reactions in the watershed, such as a decrease in ammonium ion as calcium and magnesium are produced. This would be necessary in order to maintain a chemical balance of cations and anions in the lake. This results in an increase in hydrogen ion and a lower value of alkalinity. Similarly, a decrease in bicarbonate ion, or alkalinity, may result from a decrease in both ammonium and nitrate in response to chemical weathering.

Figure 9 shows the same plot with the sum of the base cations corrected for possible additions of sodium from ocean sources. The assumption here is that all sodium associated with ocean sources is equal to the amount of chloride in the lake. This correction has a small effect on the results as the regression of the data does become closer to the expected one-to-one relationship between ANC and the sum of the base cations. This is shown by the slope of 0.8508 (R^2=0.95) as opposed to the value of 0.8071 shown in Figure 7. However, it seems that ocean sources of sodium are not very significant.

The input of acid in regions that are subject to acid deposition, beyond those from natural sources, are in such quantities that their reactions in chemical weathering are more favorable than that for carbonic acid weathering. In the case of sulfuric acid, the reaction proceeds as follows:

$$CaCO_3 + \tfrac{1}{2}H_2SO_4 <=> HCO_3^- + Ca^{2+} + \tfrac{1}{2}SO_4^{2-} \tag{37}$$
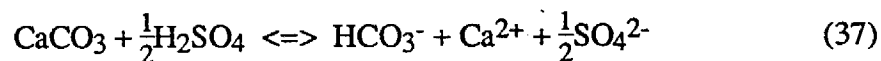
This equation explains why the scatter in Figure 9 is below the 1:1 line. The right side of Equation 37 shows that for inputs of sulfuric acid, one equivalent of ANC (HCO_3^-) is
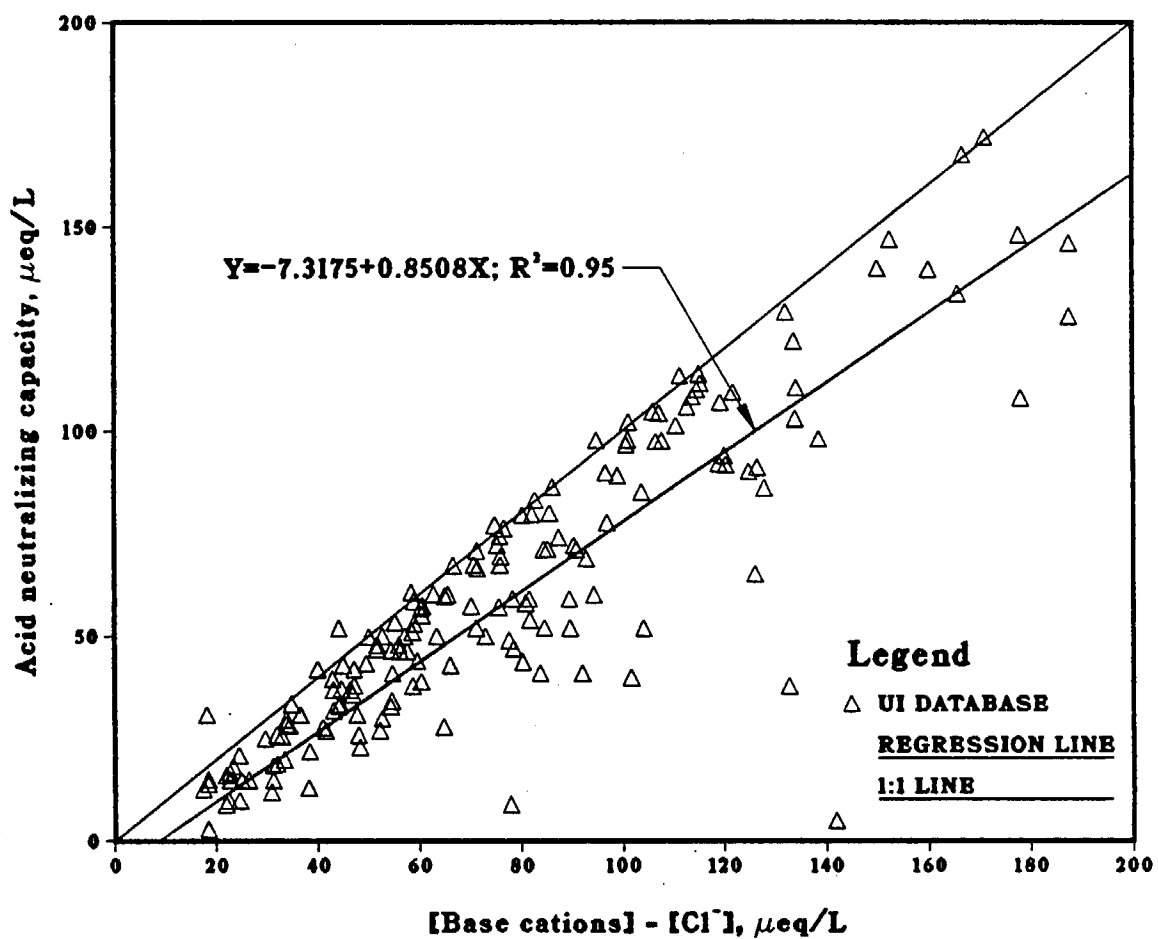
Figure 9. Acid neutralizing capacity versus the sum of the base cations corrected for
ocean sources of sodium in UI database lakes.

produced along with two equivalents of the base cation, calcium. This would shift the data from the one-to-one relationship towards the right, below the 1:1 line. Thus, Figure 9, along with Equation 37, indicates that acid deposition effects are present in the Sierra lakes.

A plot of sulfate versus the sum of the base cations (again corrected for ocean inputs of sodium) minus ANC should show a one-to-one relationship in the case that inputs of sulfuric acid had been occurring as given by Equation 37. Figure 10 shows this relationship. The data do not form a defined line but the scatter is fairly evenly distributed around the 1:1 line. If inputs of acid sources of nitrogen have also been taking place, then this same plot with the sum of sulfate and nitrate on the ordinate should give an improved one-to-one relationship. This is shown in Figure 11. Upon comparison of Figures 10 and 11, it does appear that the data has been slightly shifted upwards toward the 1:1 line. However, a chi-square analysis of the two plots shows that the better fit to the 1:1 line is for the case of Figure 10.

In an effort to be able to predict the sensitivity of Sierra lakes, ANC was plotted against various geographic data available for each lake. Melack et al. (1985) reported that this was not possible to an acceptable degree of certainty for the 73 lakes in their study. However, with the addition of the randomly generated Western Lake Survey and the Fish and Game data added to these lakes in the formation of the UI database, it was hoped that this might be possible. Linear regression analysis was performed for relationships between ANC and watershed area, lake area, and elevation. In each case, as reported by Melack et al. (1985), only a small percentage (R^2 value) of the lakes was able to show a discernable correlation between the variables. Thus this analysis proved to be inconclusive as far as predicting lake ANC from geographic characteristics.
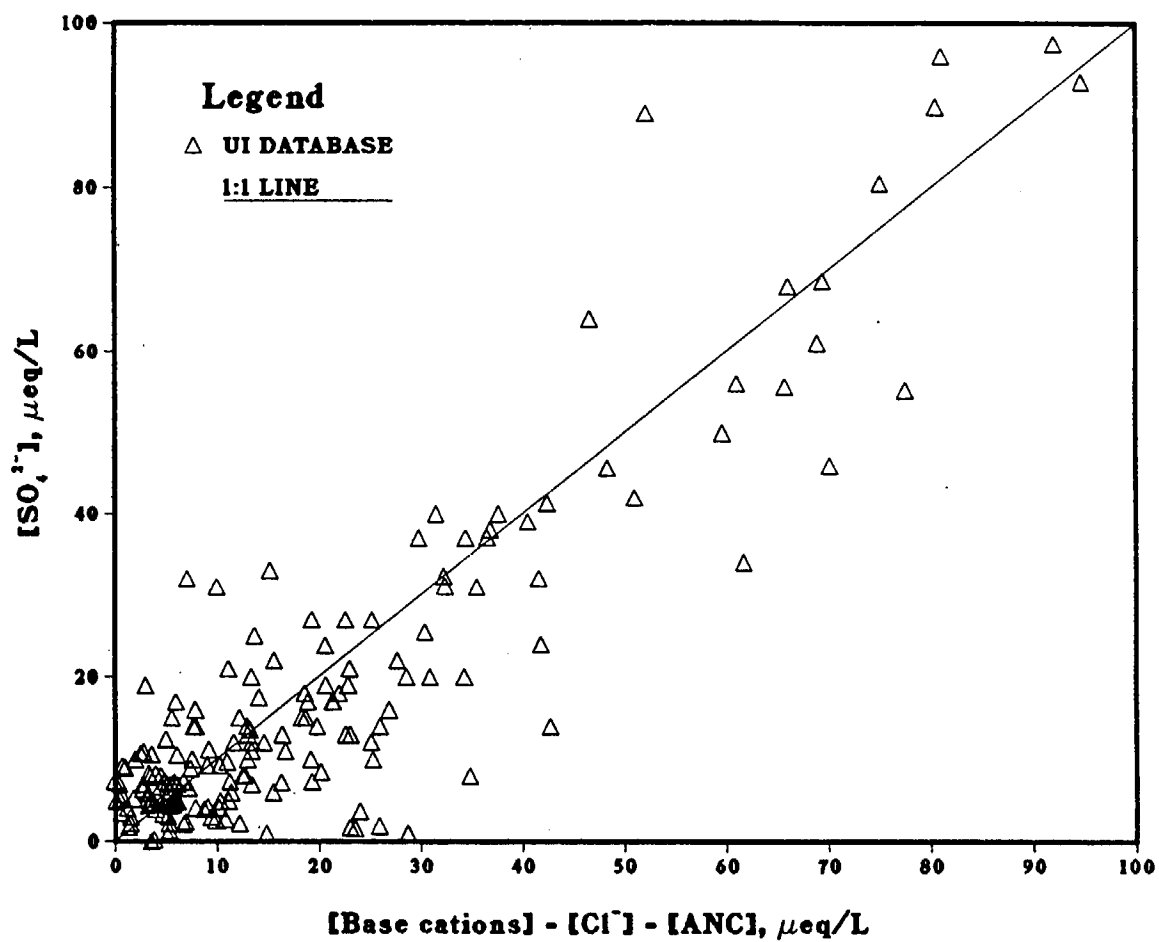
Figure 10. Lake sulfate versus the sum of the base cations (corrected for ocean sources of sodium) minus ANC.
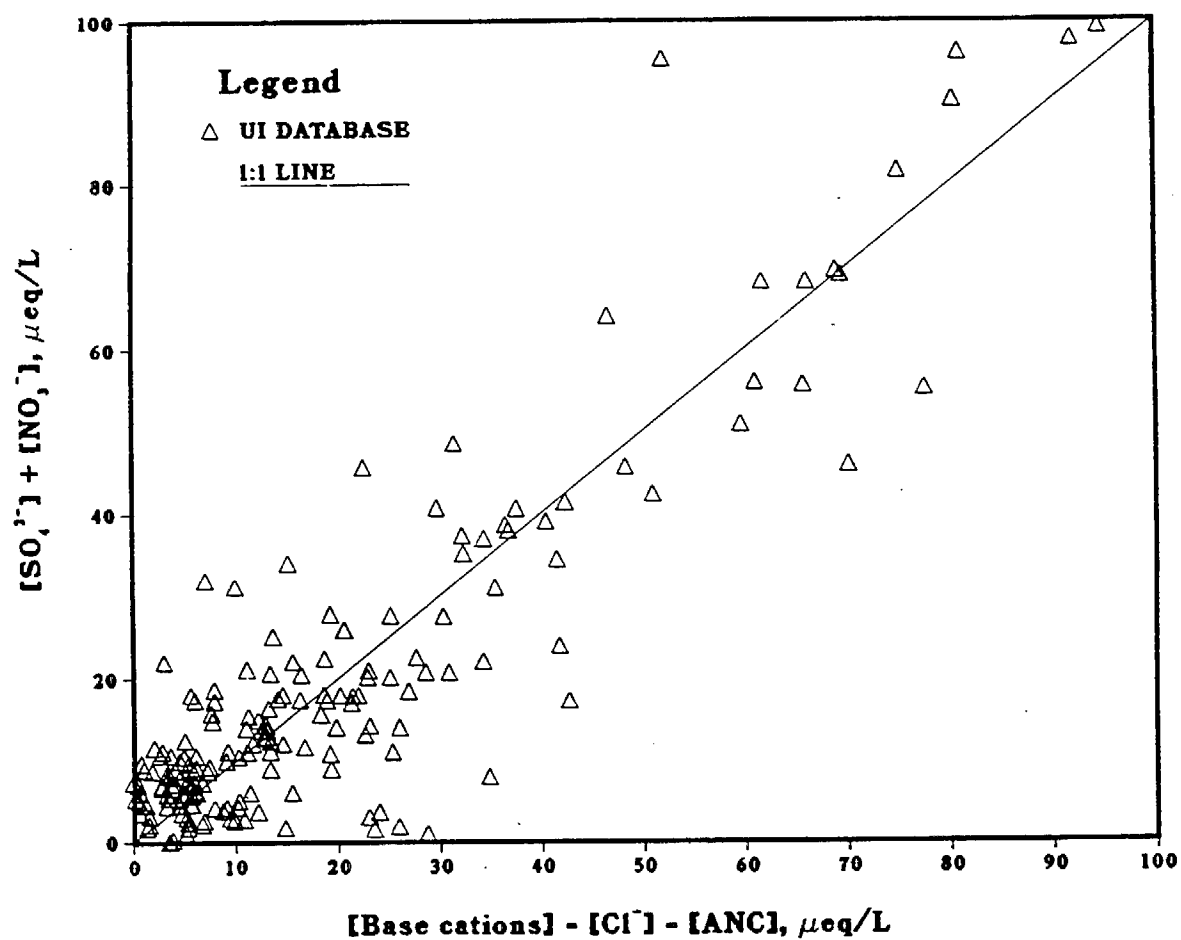
Figure 11. Lake sulfate and nitrate versus the sum of the base cations (corrected for ocean sources of sodium) minus ANC.

Lee and Schnoor (1988) Reactions Model

Frequency histograms for current RXN terms based on Equation 11 are shown in Figures

12-19. Figure 12 shows that the most frequently occurring RXN term for sulfate was -5 to

5 μeq/L. This indicates that sulfate is fairly conservative in the watershed and that sulfate

reduction is not important here. However, as stated earlier, the fact that most lakes have

RXN terms falling in the range of -5 and 5 μeq/L indicates that some lakes may have

consumption of sulfate while some lakes may produce sulfate. This produces an

uncertainty in the use of sulfate in the calculation of an evapoconcentration factor. These

reactions are a source of alkalinity in the lake as shown in Table 6.

Figures 13 and 14 show that nitrate and ammonium have a most frequently occurring

RXN term which is negative. The largest number of lakes had nitrate RXN terms of -18 to

-14 μeq/L while the greatest number of lakes consumed 21 - 15 μeq/L of ammonium. As

in the case of sulfate, nitrate consumption results in a production of ANC according to the

reactions given in Table 6. These reactions represent denitrification and nitrate assimilation

(Lin et al. 1987). Conversely, reactions which consume ammonium also consume ANC .

Ammonium reactions in the watershed occur either by nitrification or bacterial assimilation

or both. These reactions are also shown in Table 6. Figures 13 and 14 also show that the

majority of lakes consume 3-20 μeq/L of both ammonium and nitrate. This is due to the

fact that their concentrations in precipitation are very similar. Thus, according to this

analysis, the nitrogen cycle does not have a net effect on the acid status of a lake in the

Sierra at current loadings (Lee and Schnoor 1988). However, earlier it was shown that

ammonium is consumed to a greater degree than is nitrate indicating that there may be an

acidifying effect due to the nitrogen cycle.

Figures 15-19 show the results for the calcium, magnesium, sodium, chloride, and

alkalinity RXN terms, respectively. Calcium and magnesium, and to a lesser extent
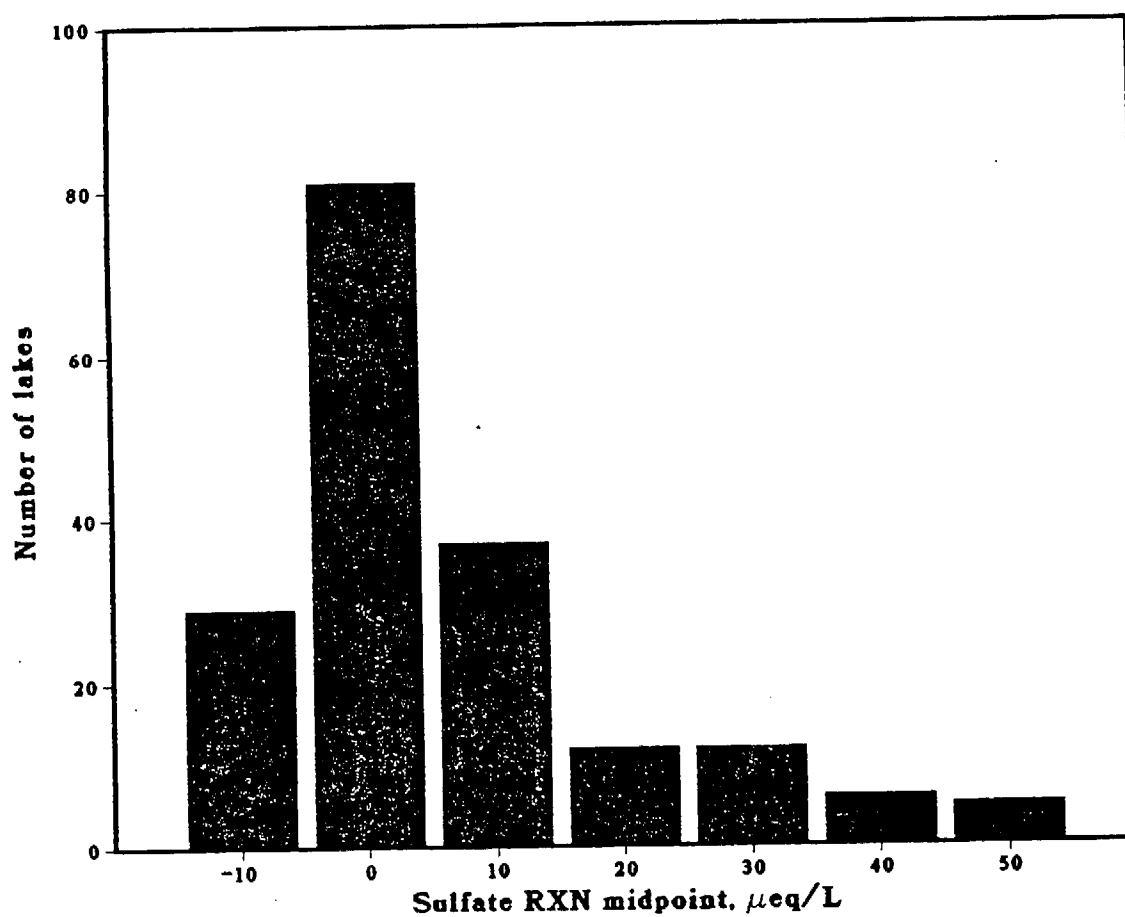
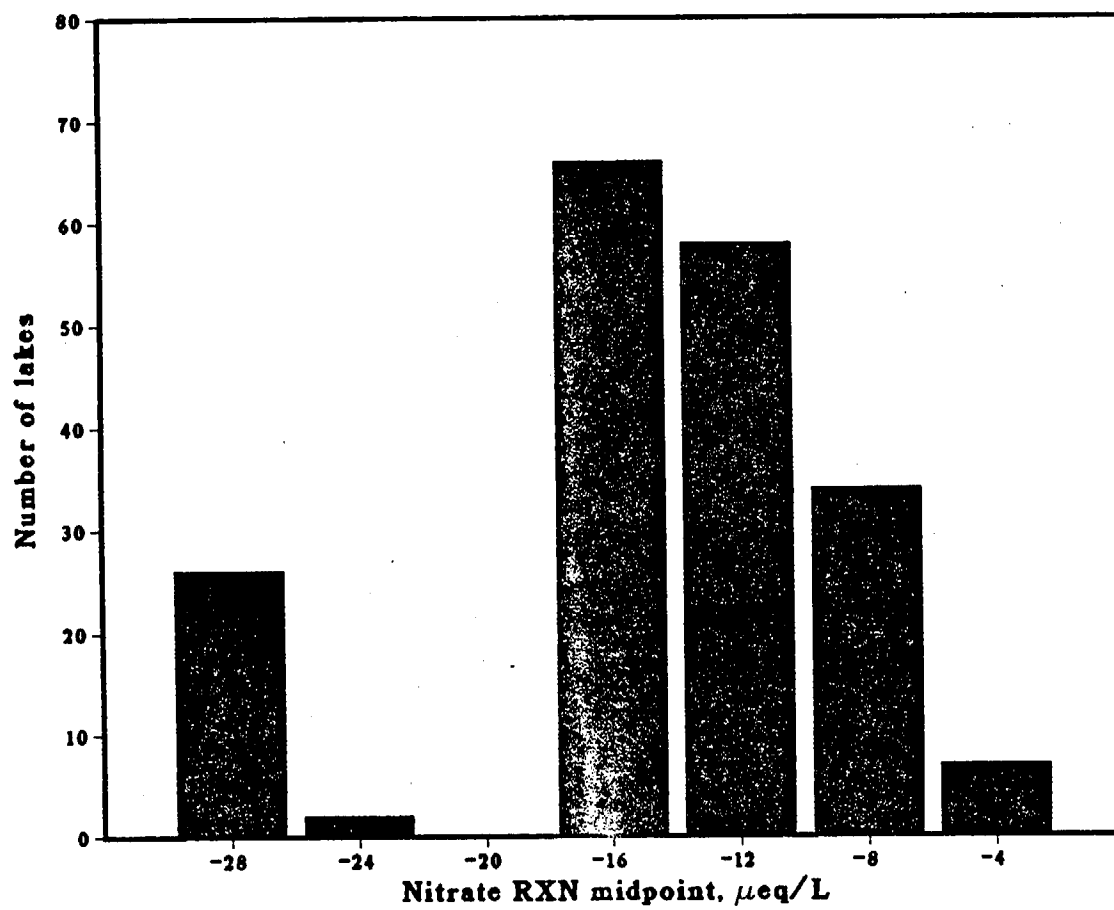Figure 12. Current sulfate reactions in lakes in the Sierra Nevada.

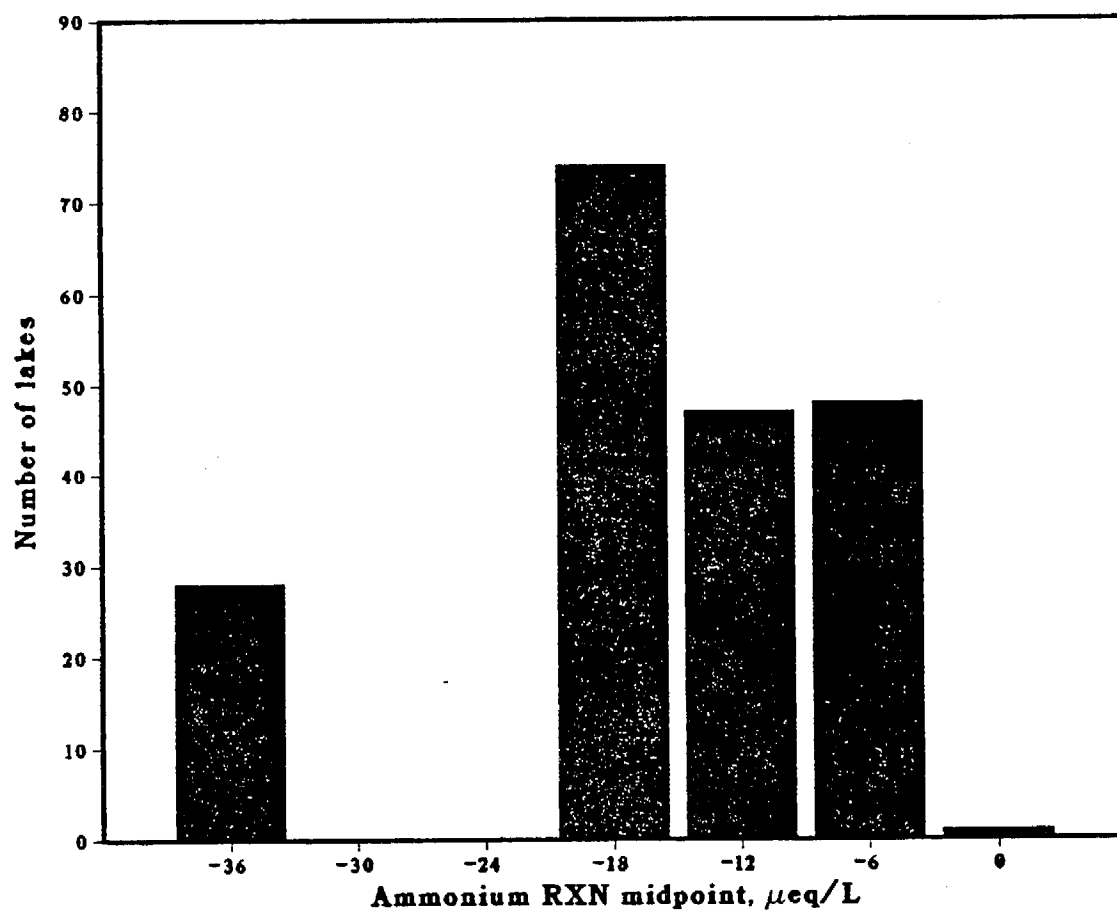Figure 13. Current nitrate reactions in lakes in the Sierra Nevada.

Figure 14.   Current ammonium reactions in lakes in the Sierra Nevada.
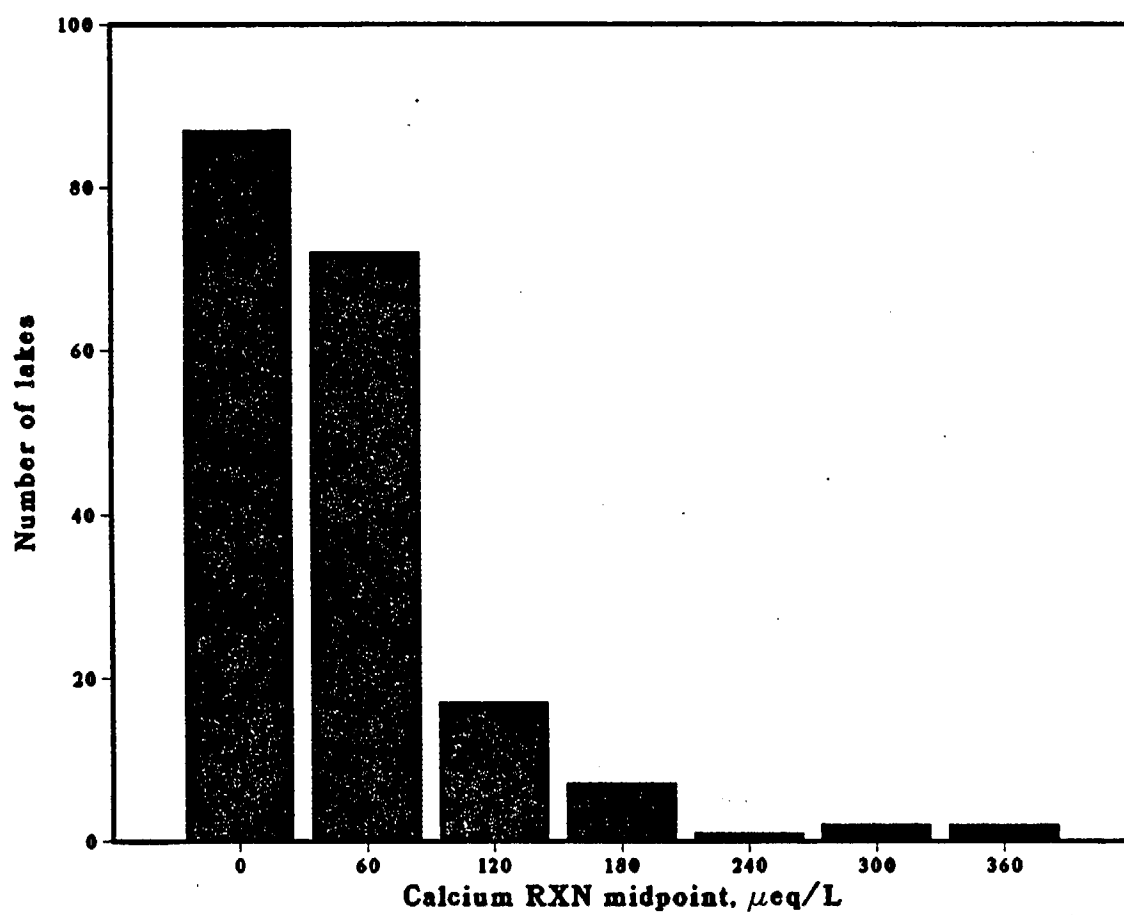
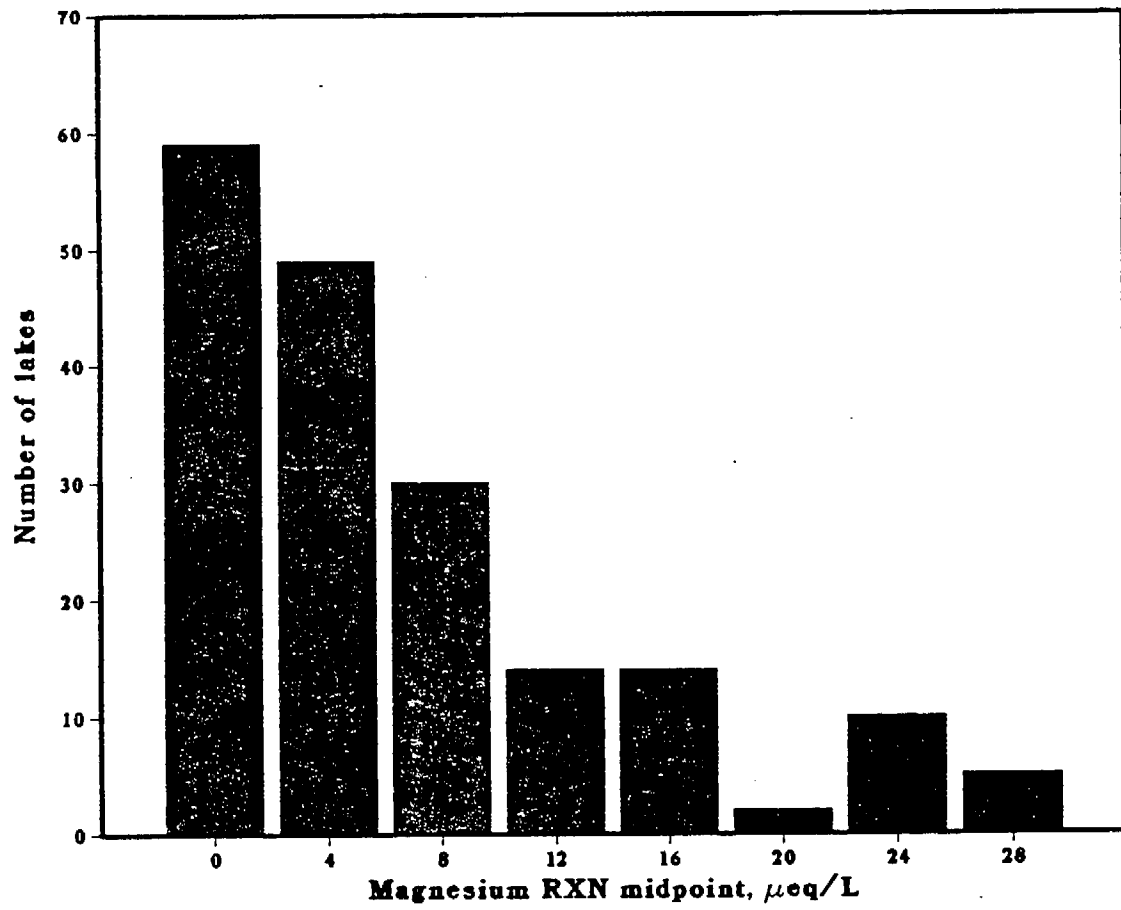Figure 15. Current calcium reactions in lakes in the Sierra Nevada.

Figure 16. Current magnesium reactions in lakes in the Sierra Nevada.

sodium, are produced in the watersheds by chemical weathering. It is evident from Figures 15 and 16 that the ability of the Sierra lakes to neutralize additions of acid by chemical weathering is weak due to the granite bedrock predominant in this mountain range. For both calcium and magnesium, the greatest number of lakes had RXN terms with a midpoint at 0 μeq/L while sodium had a most frequently occurring RXN term with a midpoint of 10 μeq/L.

Chloride ions should serve as a conservative tracer in watersheds (Lee and Schnoor 1988). The effect of marine deposits or other chloride inputs are negligible in the Sierra. Figure 18 shows that there is a slight consumption of chloride for a majority of the Sierra lakes.

Figure 19 shows the frequency histogram for the alkalinity RXN term. Sierra lakes produce some amount of alkalinity in response to current acid loadings. However, more than half of the lakes can produce only 30-90 μeq/L of alkalinity indicating that these are sensitive to increased acid loadings.

Equation 17 was used to calculate how much of each ion is consumed during biological reactions which take place in the watershed. These reactions were given in Table 6. As stated in Chapter III, the left side of Equation 17 is the fraction of a particular ion remaining in the lake after steady state has been reached. Subtracting this value from one gives the fraction of the ion that has been consumed once steady state conditions have been reached. The evapoconcentration factor in this analysis was calculated using the hydrologic data which was only available for the lakes included in the Western Lake Survey.The average ion consumption for ammonium and nitrate was then determined for these lakes.

The ion species of most interest in this study are ammonium and nitrate based on the assumptions made for the ammonium nitrate scenario to be studied as a part of the charge balance model. The average ammonium removal in the watershed was found to be 98 ±
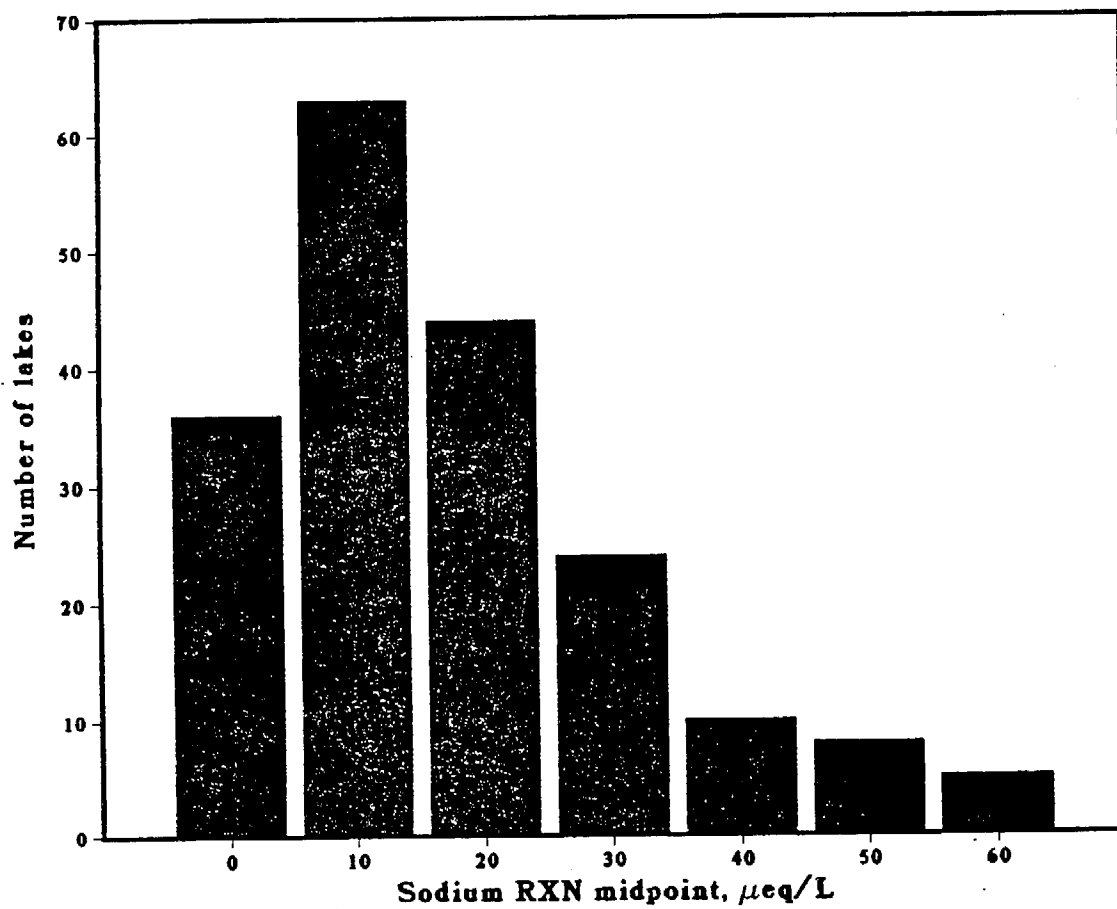
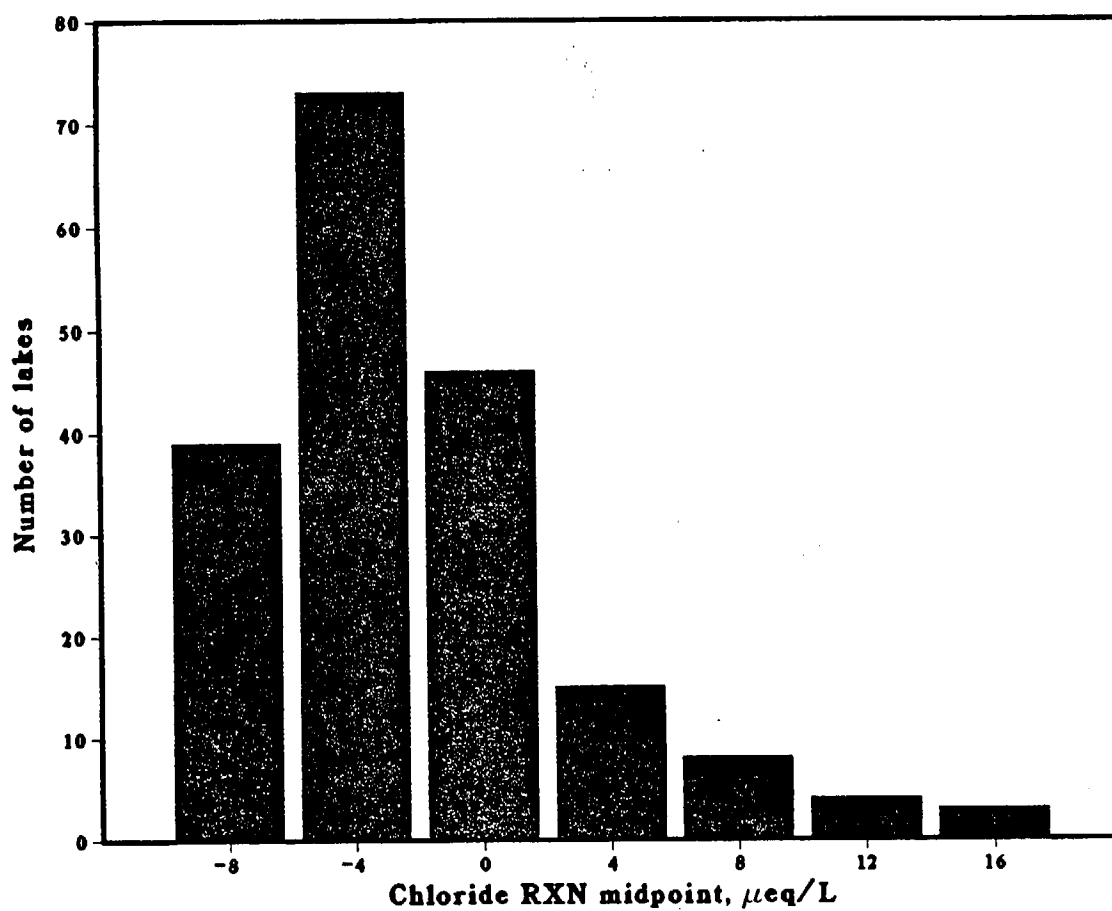Figure 17. Current sodium reactions in lakes in the Sierra Nevada.

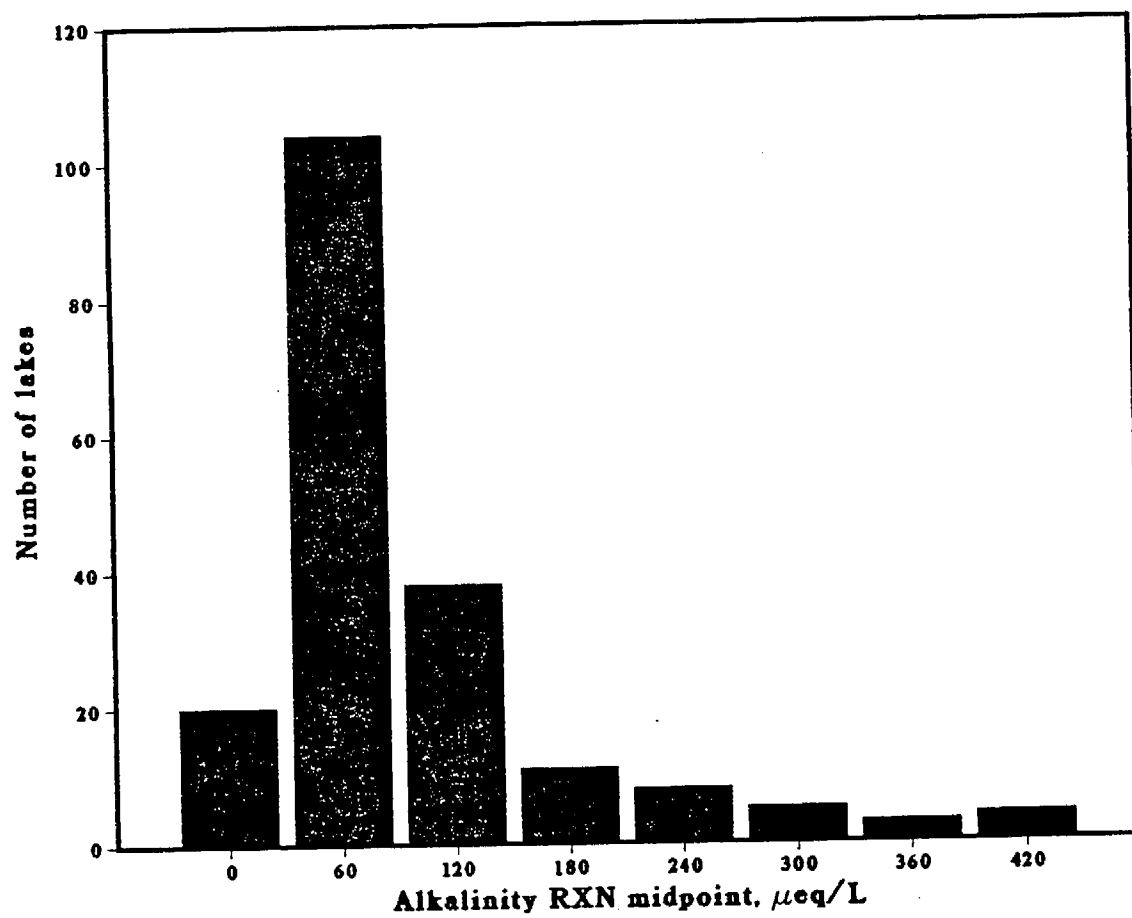Figure 18. Current chloride reactions in lakes in the Sierra Nevada.

Figure 19.   Current alkalinity reactions in lakes in the Sierra Nevada.

5% while the average removal for nitrate was 93 ± 11%. Thus the assumptions that ammonium is 100% reacted and nitrate is only partially reacted are valid.

As stated in Chapter III, there is a possible error in this scenario. This is due to the assumption that all the ammonium in the watershed is consumed by plant uptake. The error is introduced if all or part of the ammonium is consumed by nitrification. It was stated that the maximum possible error in this case would be equal to 1-R, where R is the fraction of nitrate removed by biological reactions. Thus, from the previous analysis, the value of this maximum possible error is 7%.

Henriksen and Thompson Models

The present condition of UI database lakes according to Henriksen's nomograph is shown in Figure 20. The model shows that currently there are no acid lakes. There are, however, six lakes which fall into the sensitive category. Figure 7 indicated that 38% of the UI database lakes have an ANC ≤ 50 μeq/L. This may be an indication that the effects of nitrate are such that the Henriksen nomograph cannot accurately predict lake sensitivity due to its assumptions. This is probably in part due to the fact that this model was empirically derived from over 700 Norwegian lakes. It may be this model does not apply to lakes in the Sierra.

The results of Henriksen's and Thompson's models are summarized in Table 7. Figures 21-23 show the predictive results of Henriksen's nomograph for F-factors of 0.6, 0.4 and 0.2, respectively, for double loadings of sulfate. Twice the current levels of sulfate with an F-factor of 0.6 results in 5% sensitive lakes including 1% acidic lakes. An F-factor of 0.2, as expected, results in a greater number of sensitive (11%) and acidic (3%) lakes. In each of the three plots shown for double loading, there are a number of lakes
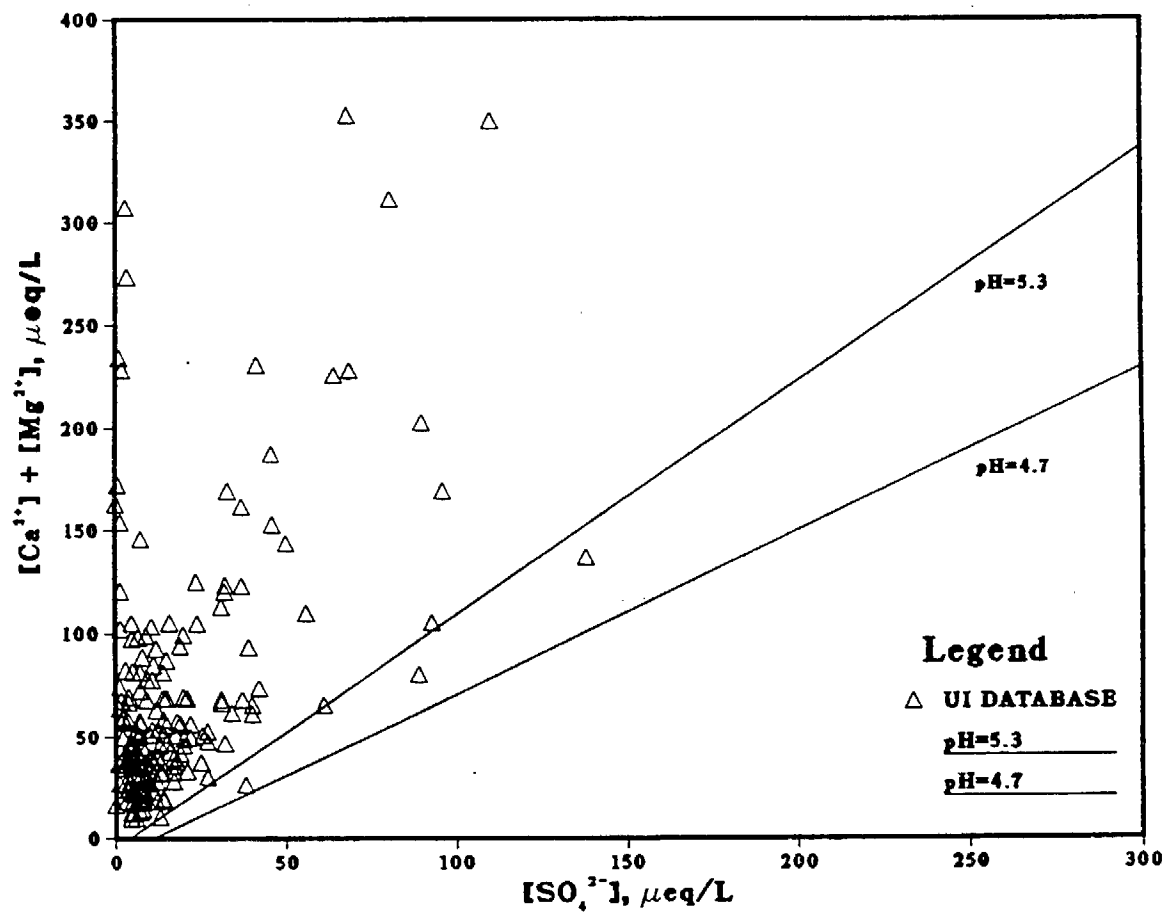
Figure 20.   Use of Henriksen's nomograph (developed using over 700 Norwegian
lakes)to show the present condition of UI database lakes

very near to the pH = 5.3 line, or the transition zone. Thus, many more lakes would enter this zone as they lose their buffering capacity through increased sulfate loadings.

Figures 24-26 show the cases for half the current sulfate concentrations in the lake for the same F-factors. In each case except that for F=0.6, all the currently sensitive lakes regain sufficient buffering capacity to be classified as alkaline. It seems from these plots that reductions in acid (sulfate in this case) to the lake have a greater effect on the chemical condition of the lakes. More lakes become less acidic with decreases in lake sulfate than the number of lakes that become sensitive or acidic with increases in lake sulfate.

Thompson's model is similar to Henriksen's but essentially assumes what is equivalent to an F-factor of zero. Figures 27 and 28 show the distribution of lakes for double and half sulfate loadings, respectively, of existing lake sulfate. The results here are similar to the Henriksen's plots as half loading does not result in any lakes entering the acid or sensitive categories, while double loading causes 21% of the lakes to become sensitive with 7% being acid.

Steady State Charge Balance Model

Predictive Results

Figure 29 shows the results for the predicted ANC of the lakes under changes in deposition sulfuric acid plotted as a cumulative proportion. Lakes with alkalinities of 0 to 40 μeq/L are considered to be sensitive to increased acid loadings, while lakes with an ANC less than zero are termed acidic. Presently, 29% of the UI database lakes are sensitive by this definition. An increase of 100%, twice the current sulfuric acid loading (based on deposition sulfate), caused 35% of the database lakes to become sensitive with 1% becoming acidic. A reduction in sulfuric acid loading of 50% resulted in fewer lakes in

Table 7. Percentage of sensitive lakes resulting from changes in sulfate loadings derived from the Henriksen and Thompson models with the percentage of acid lakes in parentheses.

F-factor	Percentage of Sensitive Lakes (% Acid Lakes)	
	Double (+100%) Loading	Half (-50%) Loading
Present	2% (0%)	
0.6	5% (1%)	0% (0%)
0.4	9% (2%)	0% (0%)
0.2	11% (3%)	0% (0%)
0.0	21% (7%)	0% (0%)
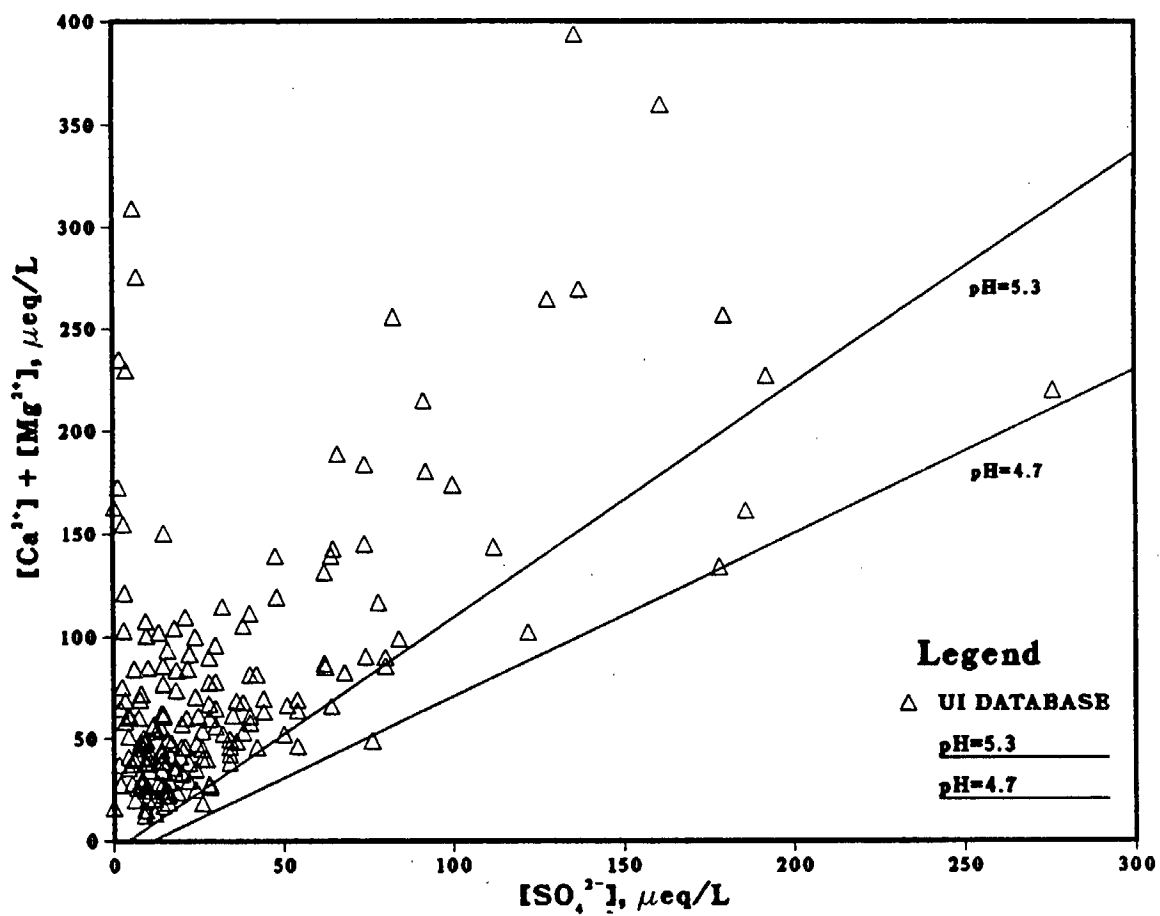
Figure 21. UI database lake data fitted to Henriksen's nomograph with an F-factor of 0.6 and double the current lake sulfate concentrations.
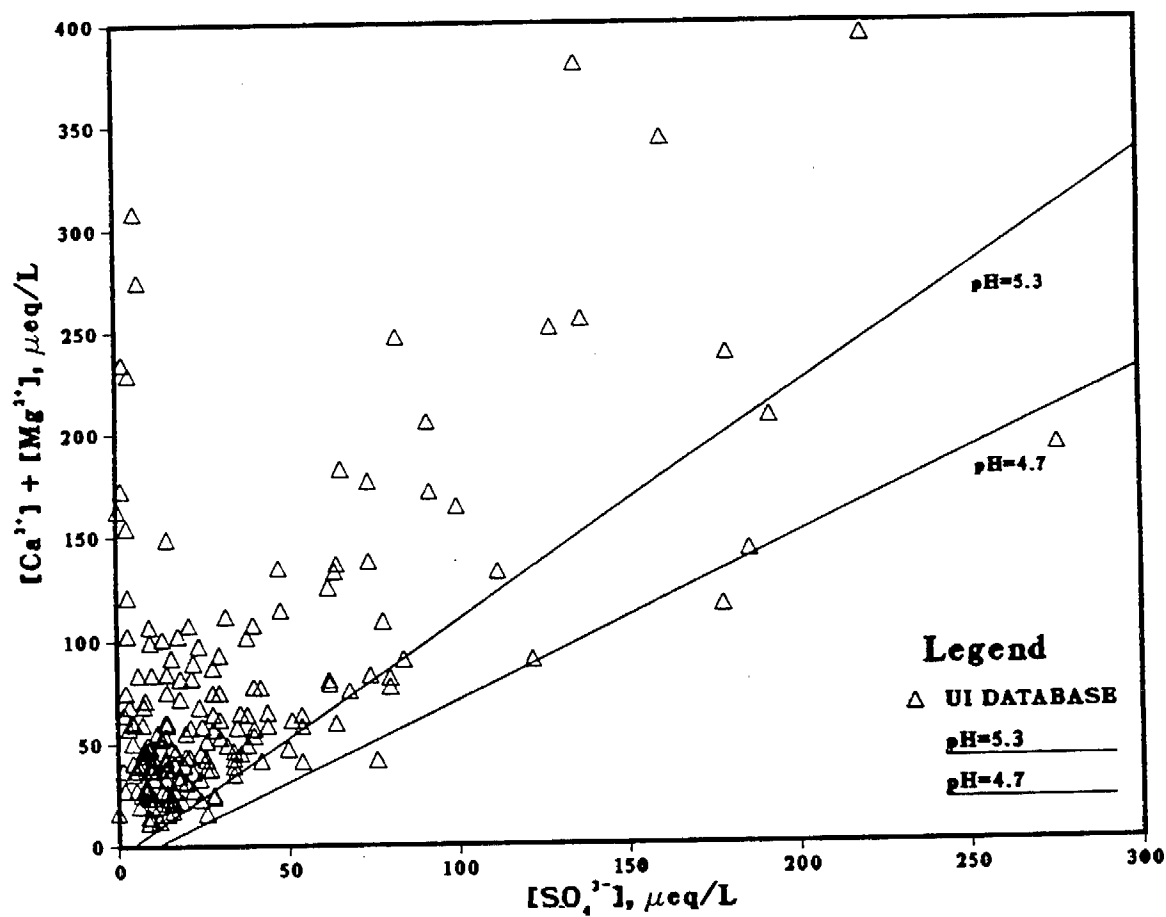
Figure 22. UI database lake data fitted to Henriksen's nomograph with an F-factor of
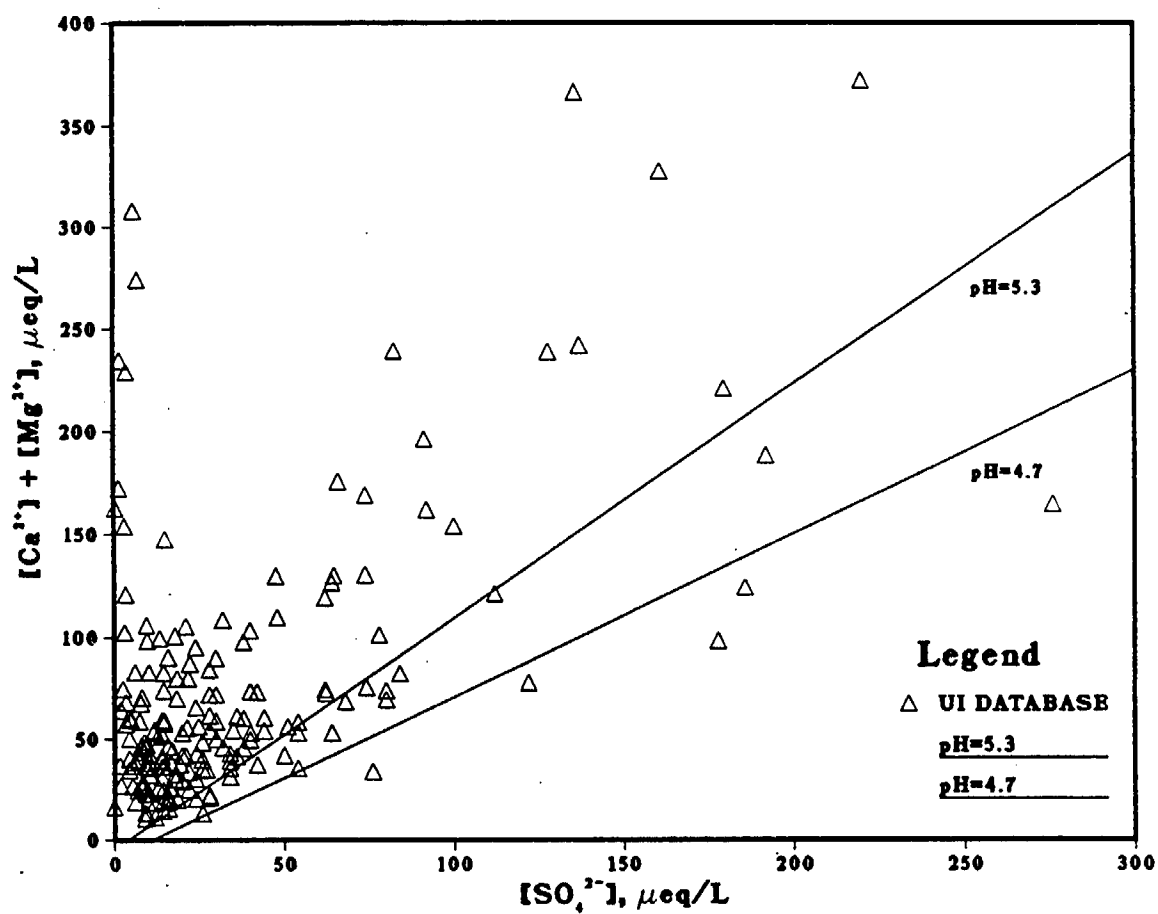0.4 and double the current lake sulfate concentrations.

Figure 23.   UI database lake data fitted to Henriksen's nomograph with an F-factor of 0.2 and double the lake current sulfate concentrations.
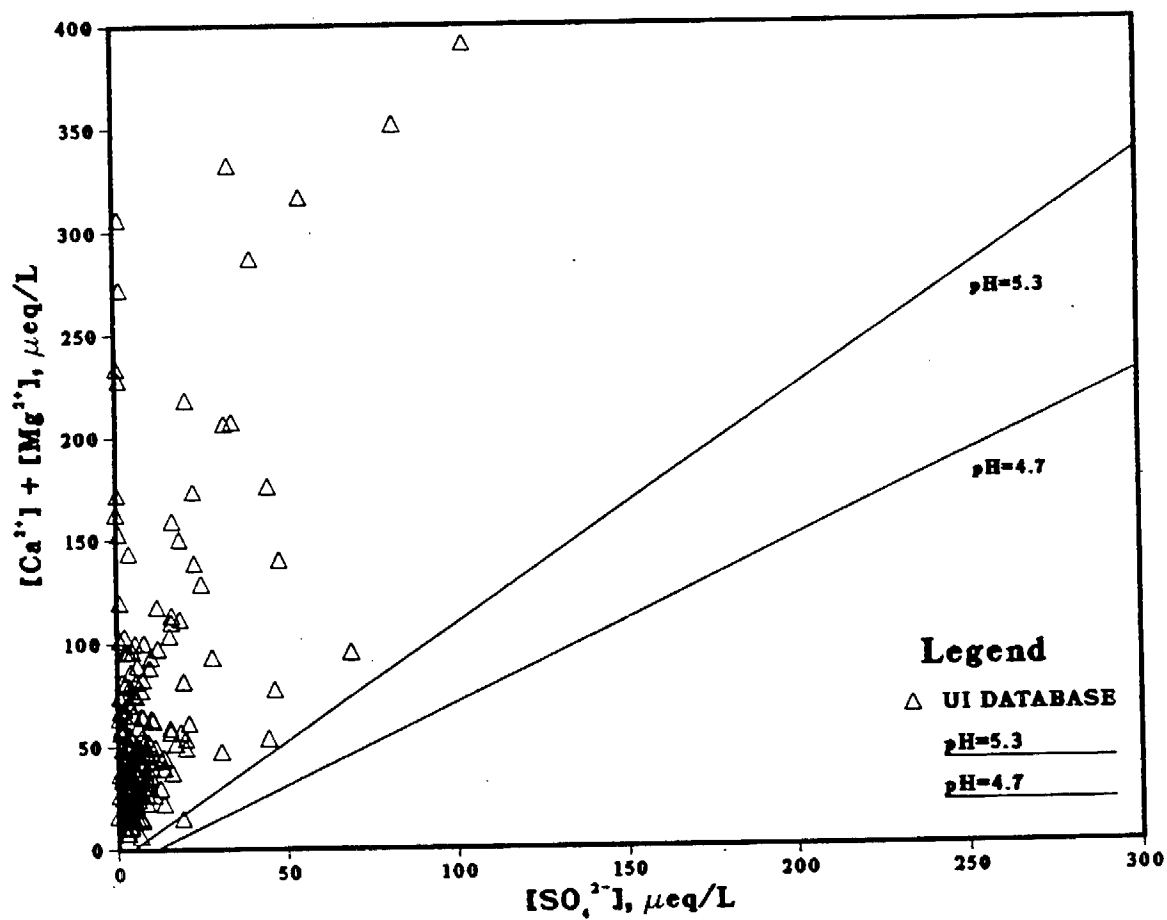
Figure 24.   UI database lake data fitted to Henriksen's nomograph with an F-factor of 0.6 and half the lake current sulfate concentrations.
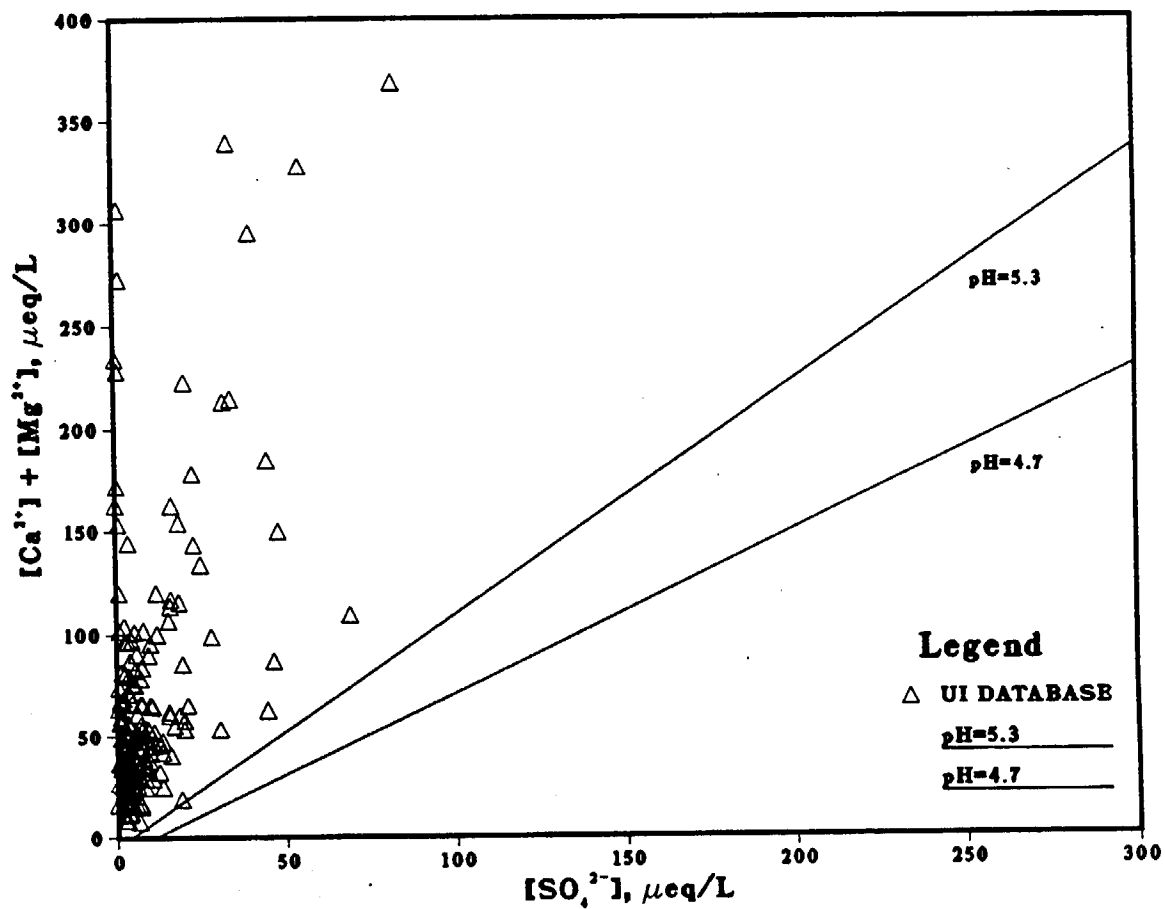
Figure 25.   UI database lake data fitted to Henriksen's nomograph with an F-factor
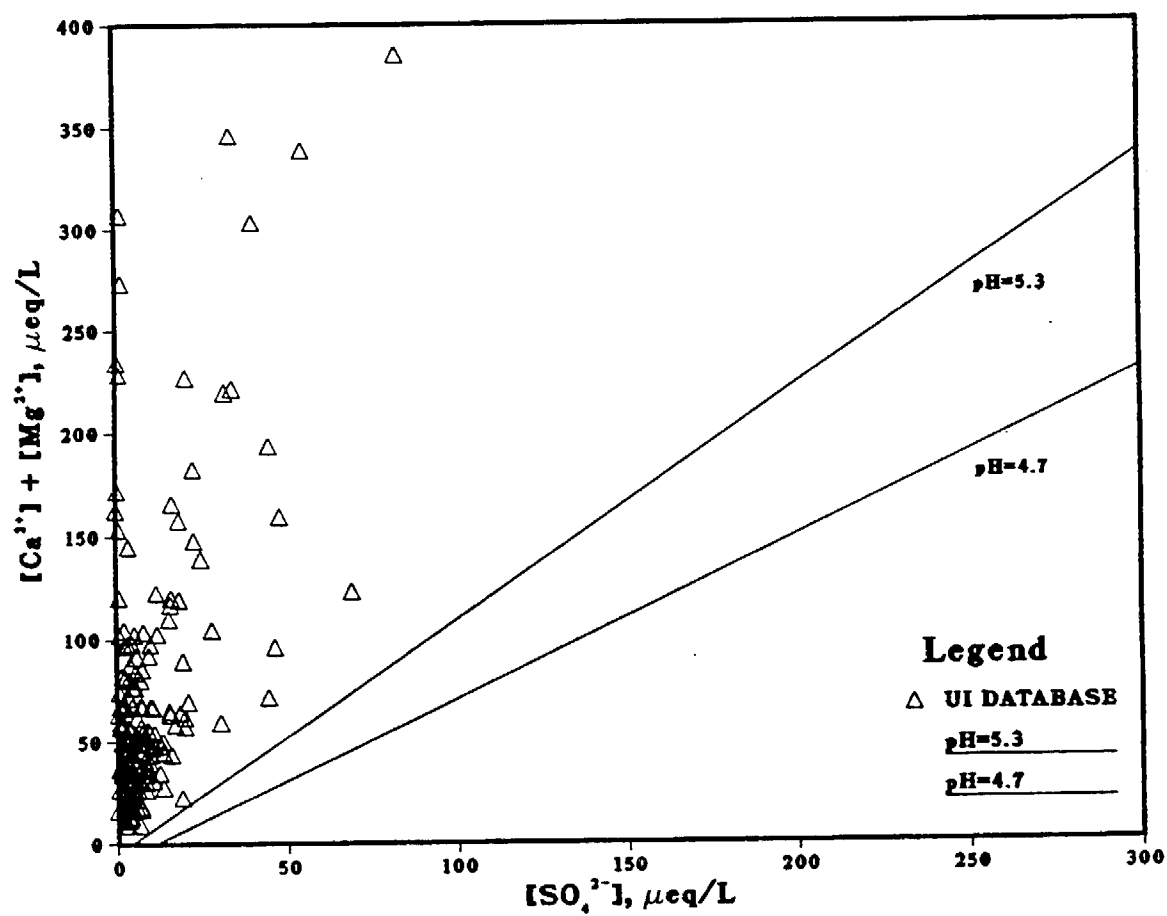of 0.4 and half the lake current sulfate concentrations.

Figure 26.   UI database lake data fitted to Henriksen's nomograph with an F-factor
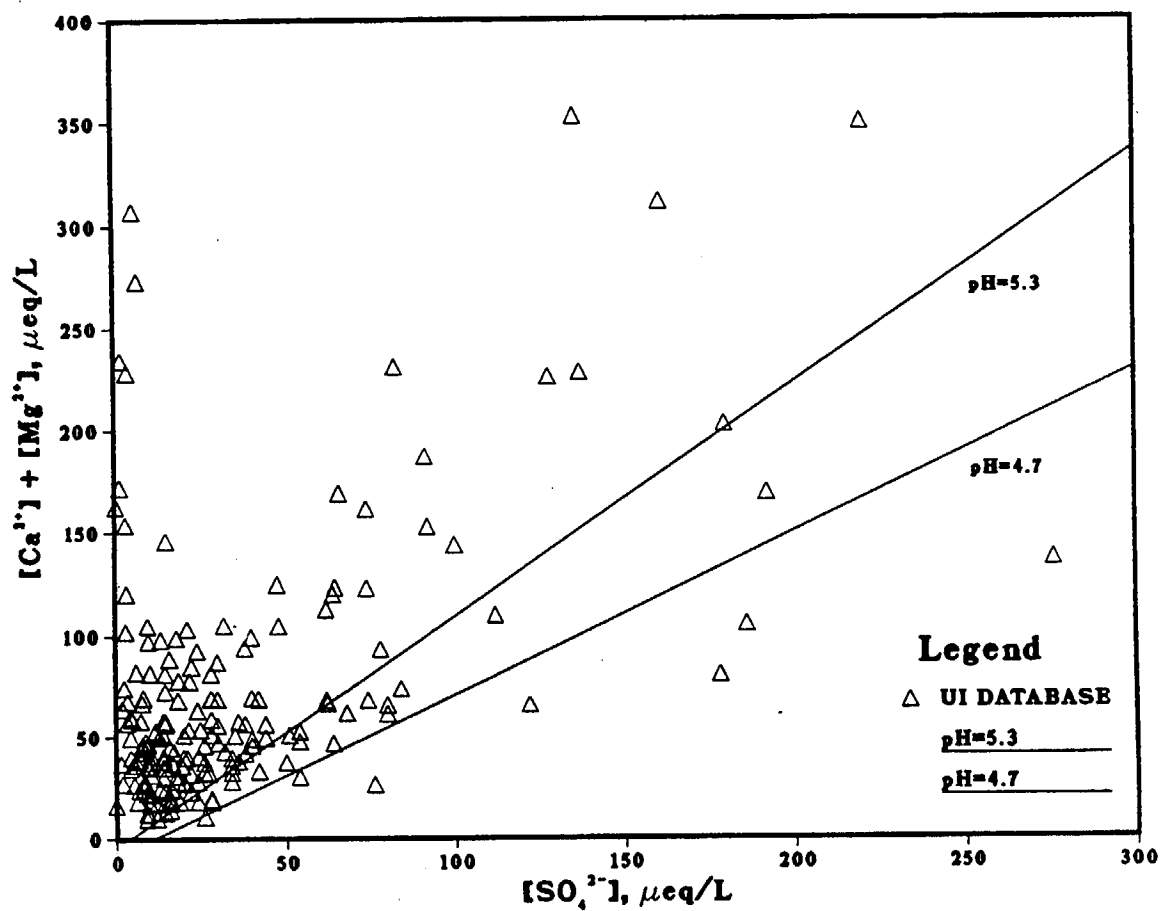   of 0.2 and half the lake current sulfate concentrations.

Figure 27. UI database lake data fitted to Henriksen's nomograph with an F-factor of 0.0 (Thompson) and double the lake current sulfate concentrations.
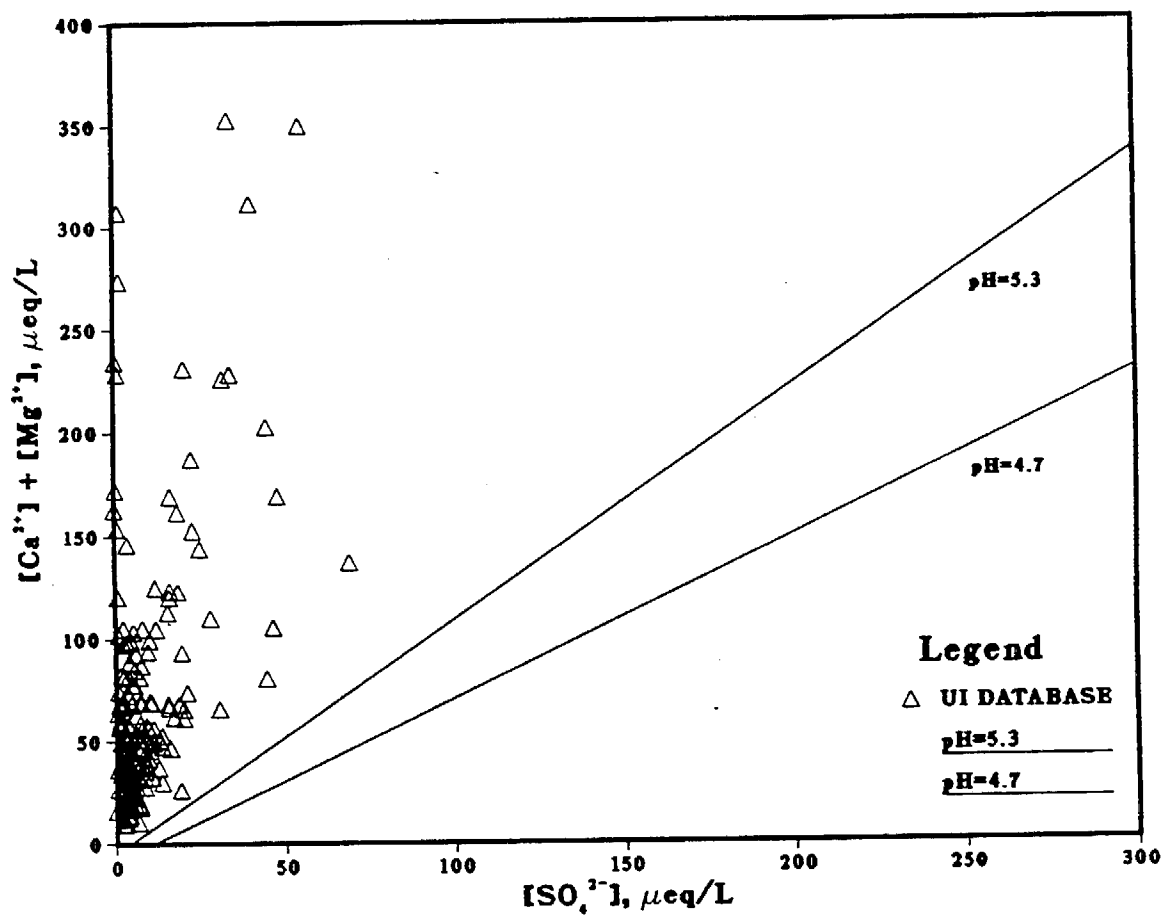
Figure 28.   UI database lake data fitted to Henriksen's nomograph with an F-factor of 0.0 (Thompson) and half the lake current sulfate concentrations.

the sensitive category. A sulfuric acid loading equal to half of the current levels (50% reduction) resulted in 26% sensitive lakes.

Figure 30 shows the changes in ANC in a histogram format. At lower alkalinities it is evident that the number of lakes in the 40 µeq/L range (20 to 60 µeq/L) changes depending on whether deposition loadings are being increased or decreased. Beyond 40 µeq/L the bar diagram is slightly misleading as some lakes will move from one range while others move into that same range. In other words, some ranges above 40 µeq/L will not show a change in the number of lakes in that ANC range or may show a decrease in number for an increase in acid deposition. At the lower ranges, especially in the range of -20 to 20 µeq/L, the number of lakes will always increase with increases in acid and decrease with decreases in acid.

We also wanted to look at each scenario for the case of a wet and a dry precipitation season. Figures 31 and 32 show the results of this analysis for a dry year and a wet year, respectively. The percentage of sensitive lakes in a dry year for an increase of 100% in sulfuric acid changes to 35% as opposed to 35% for the normal case shown in Figure 29. This number decreases to 24% for half of the current deposition of sulfuric acid as opposed to 26% in a normal precipitation year. Figure 30 shows that in a wet year, the number of sensitive lakes (33%) is less than for normal rainfall conditions (see Figure 29) for a double loading of sulfuric acid. The number of sensitive lakes under decreased sulfuric acid loading is about the same as for normal rainfall conditions. Thus the amount of precipitation in a particular season has a slight effect on the number of lakes in the category when there are additional inputs of acid deposition. In a dry year, the change in sulfuric acid loading will have a greater effect on the chemical condition of a lake, i.e. more lakes will become sensitive to increases in acid loading and less sensitive to decreases in acid loading, than in a wet year. This is due to the fact that more evaporation takes place and
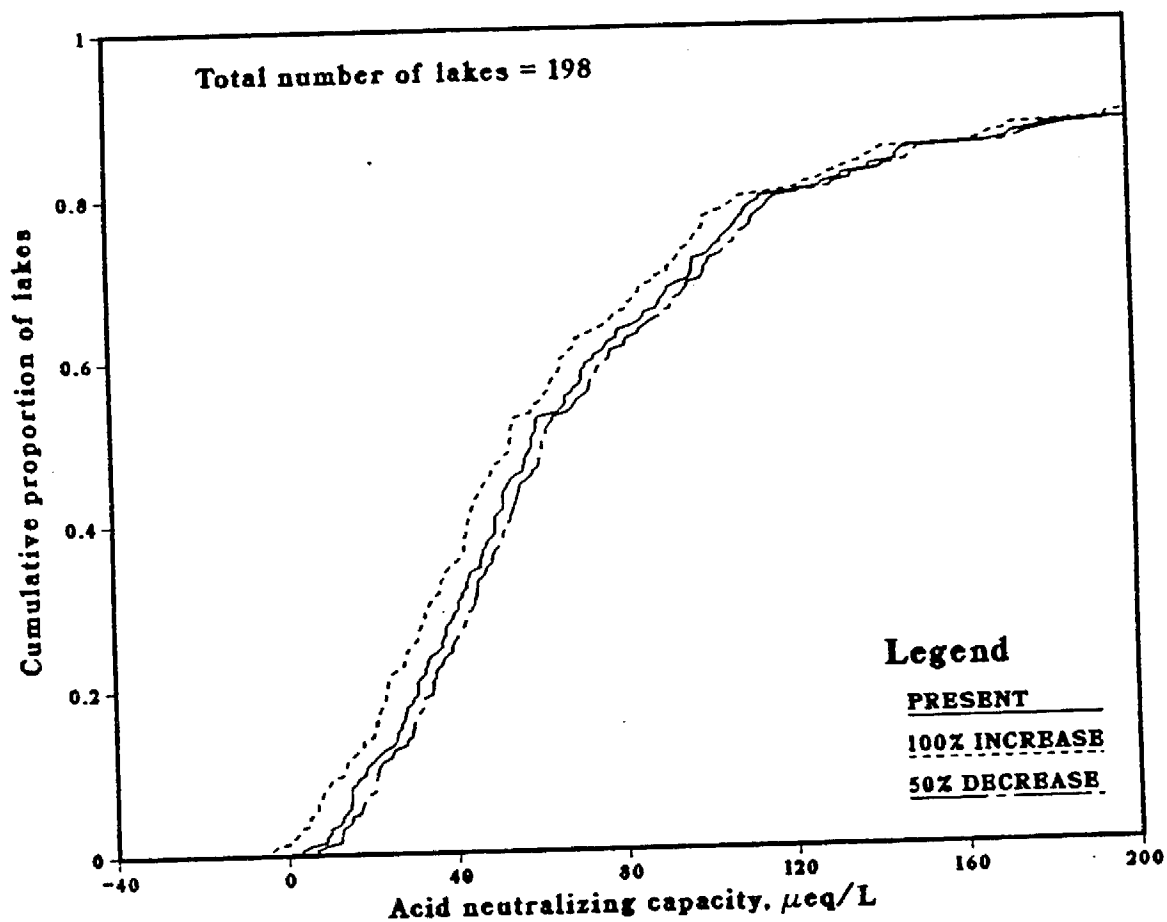
Figure 29. Steady state charge balance model predicted chemical condition of UI database lakes due to changes in sulfuric acid loadings.
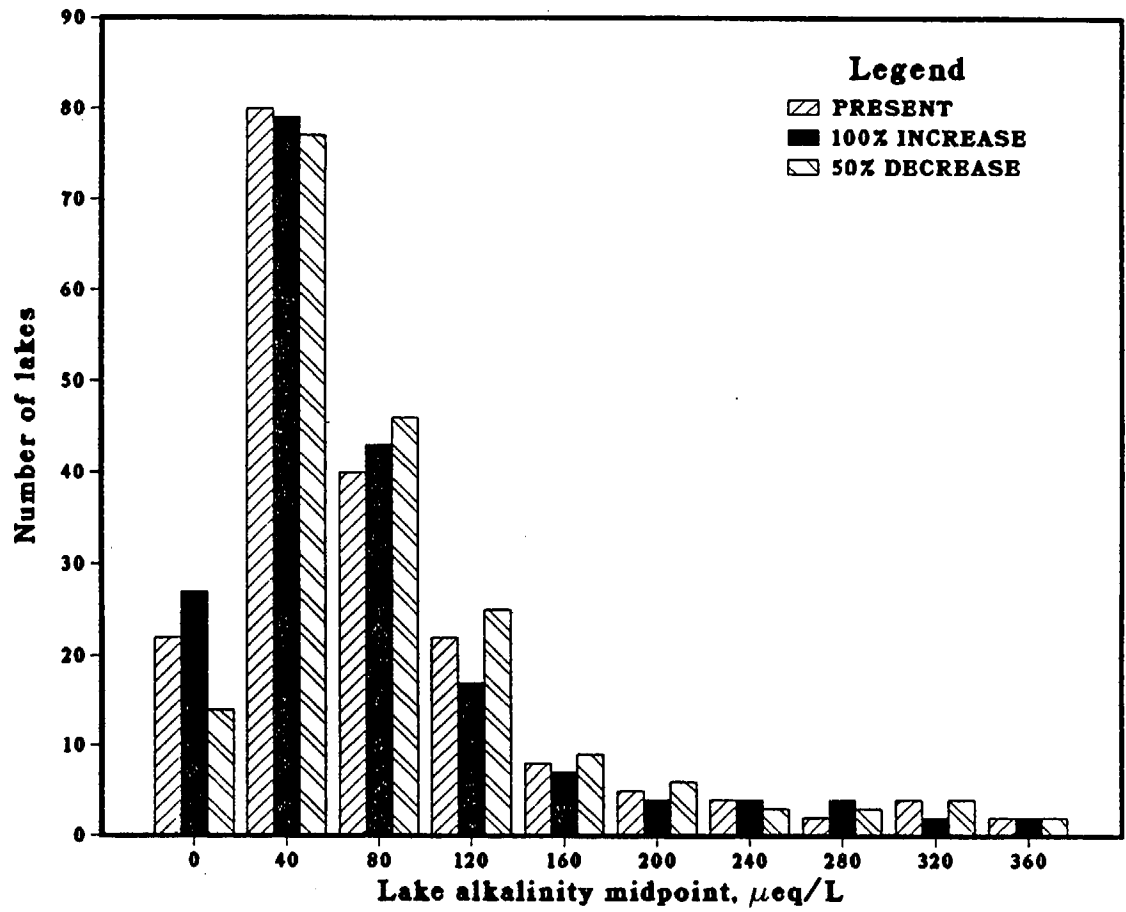
Figure 30. Histogram showing the number of lakes with predicted ANC values using the steady state charge balance model for changes in sulfuric acid loadings.
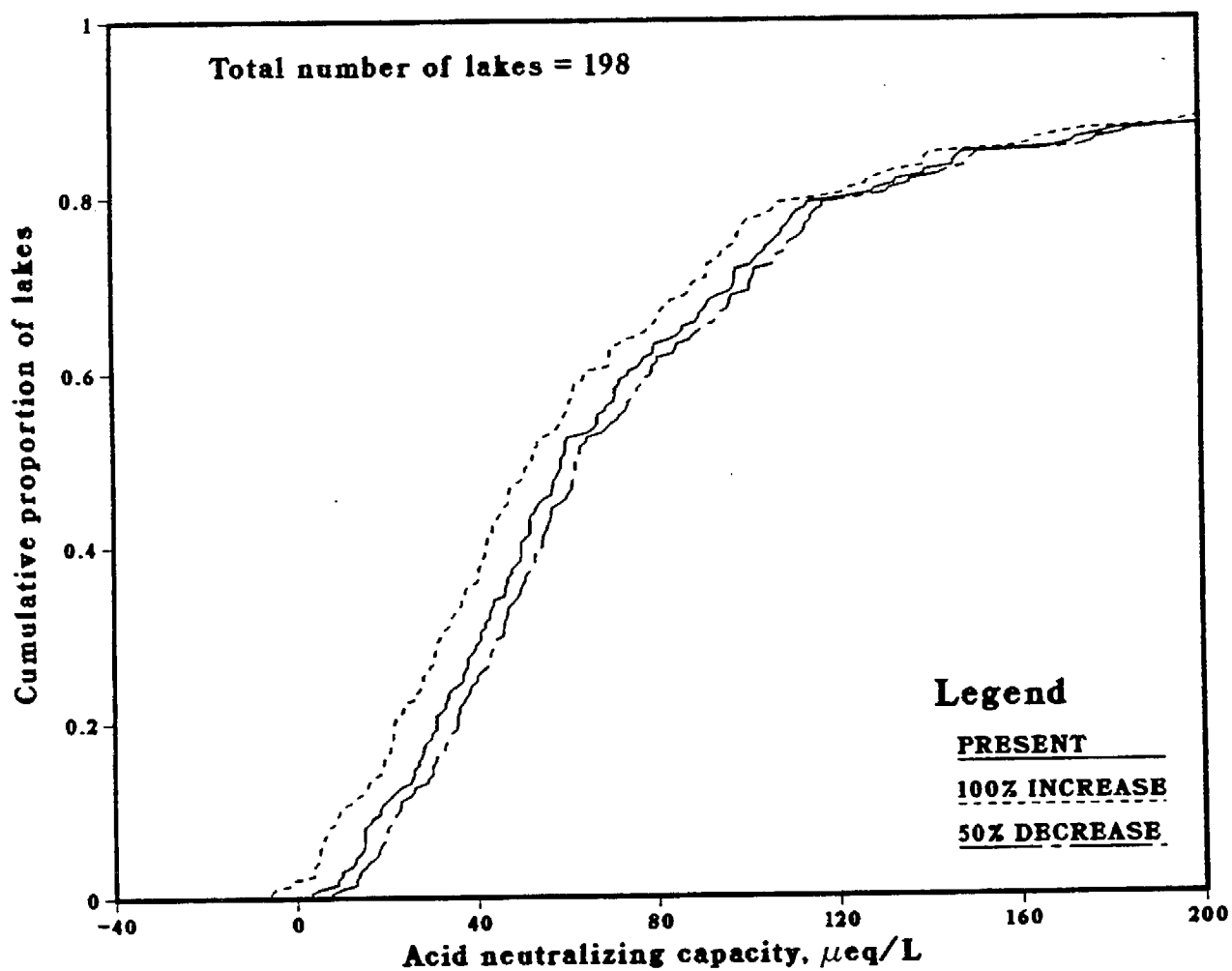
Figure 31.   Predicted chemical condition of UI database lakes due to changes in sulfuric acid loadings in a dry year using the steady state charge balance model.
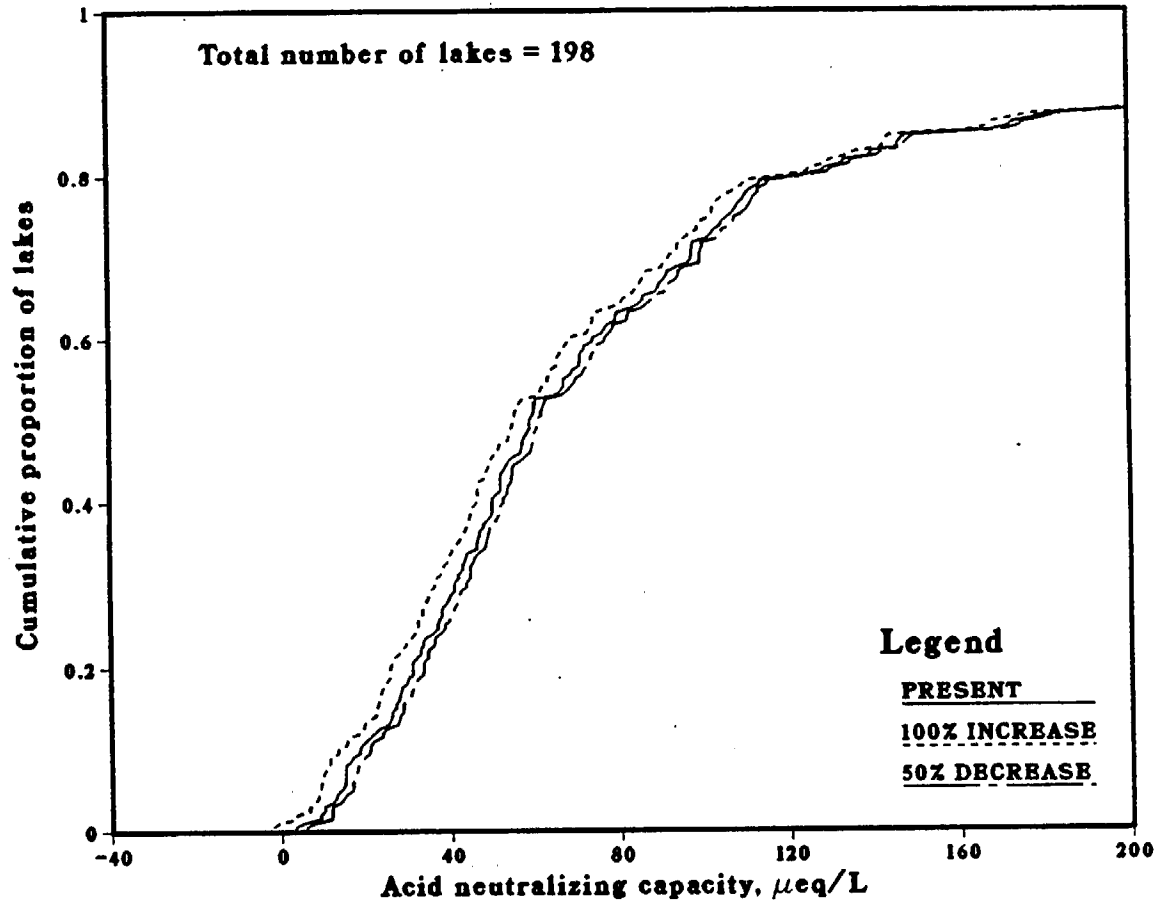
Figure 32. Predicted chemical condition of UI database lakes due to changes in sulfuric acid loadings in a wet year using the steady state charge balance model.

there is less dilution with the lesser amount of rainfall, thus making the deposition ion species more concentrated in the lake.

Figure 33 shows the results for changes in ammonium nitrate loadings. The effects for double and half loadings are less than those found in the sulfuric acid scenario. An increase of 100% in current deposition loading resulted in 31% sensitive lakes. This compares to 35% for the same loading in the sulfuric acid scenario. Similarly, a decrease of 50% in current deposition loading produced 27% sensitive lakes. The same loading in the sulfuric acid scenario resulted in 26% sensitive lakes. This would indicate that ammonium nitrate loadings are of lesser importance than those of sulfuric acid. Figure 34 shows these results in histogram format.

The results for dry and wet seasons are shown in Figures 35 and 36. As in the case of a normal precipitation year, the number of sensitive lakes in the dry year for changes in this scenario is less than the number found in the dry year case for the sulfuric acid scenario. A double loading of ammonium nitrate causes more lakes to become sensitive (31%) than an equal increase in sulfuric acid (35%). There is only one acid lake (ANC ≤ 0 μeq/L) for this loading. It would seem that changes in ammonium nitrate loadings have a lesser effect on the chemical condition of a lake than do changes in deposition sulfuric acid.

Wet year results for changes in ammonium nitrate follow the same trend. The percentage of sensitive lakes with a 100% increase was 30%. No lakes had ANC values less than zero. Decreases in ammonium nitrate loadings do not decrease the number of sensitive lakes (28%) as much as does the same decrease in sulfuric acid (26%), again indicating that this scenario does not affect the ANC of a lake to the same magnitude as does changes in sulfuric acid loadings.

The model is sensitive to the ratio of NH_4^+/NO_3^- in deposition. If the ratio is significantly greater than 1:1 in future deposition, the effects on lake ANC due to
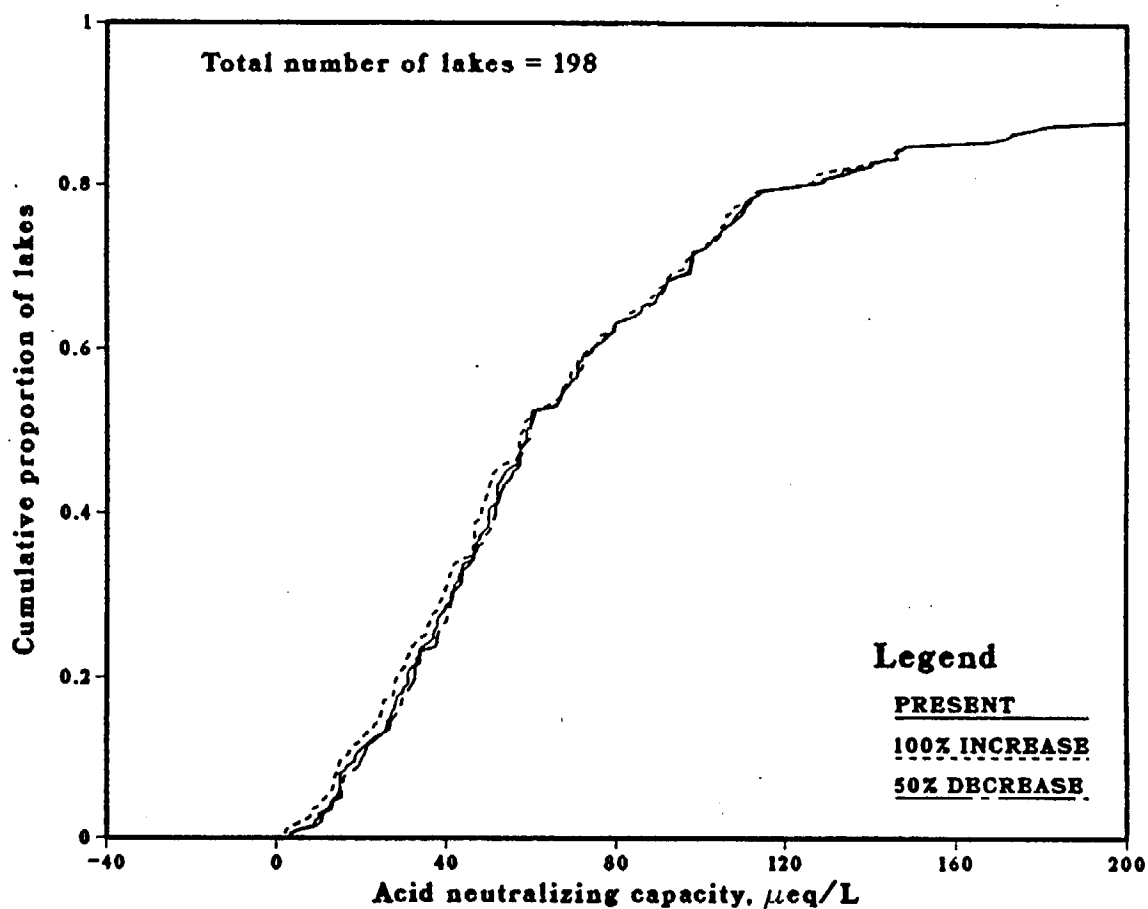
Figure 33. Steady state charge balance model predicted chemical condition of UI database lakes due to changes in ammonium nitrate loadings (NH_4^+/NO_3^- = 1:1).
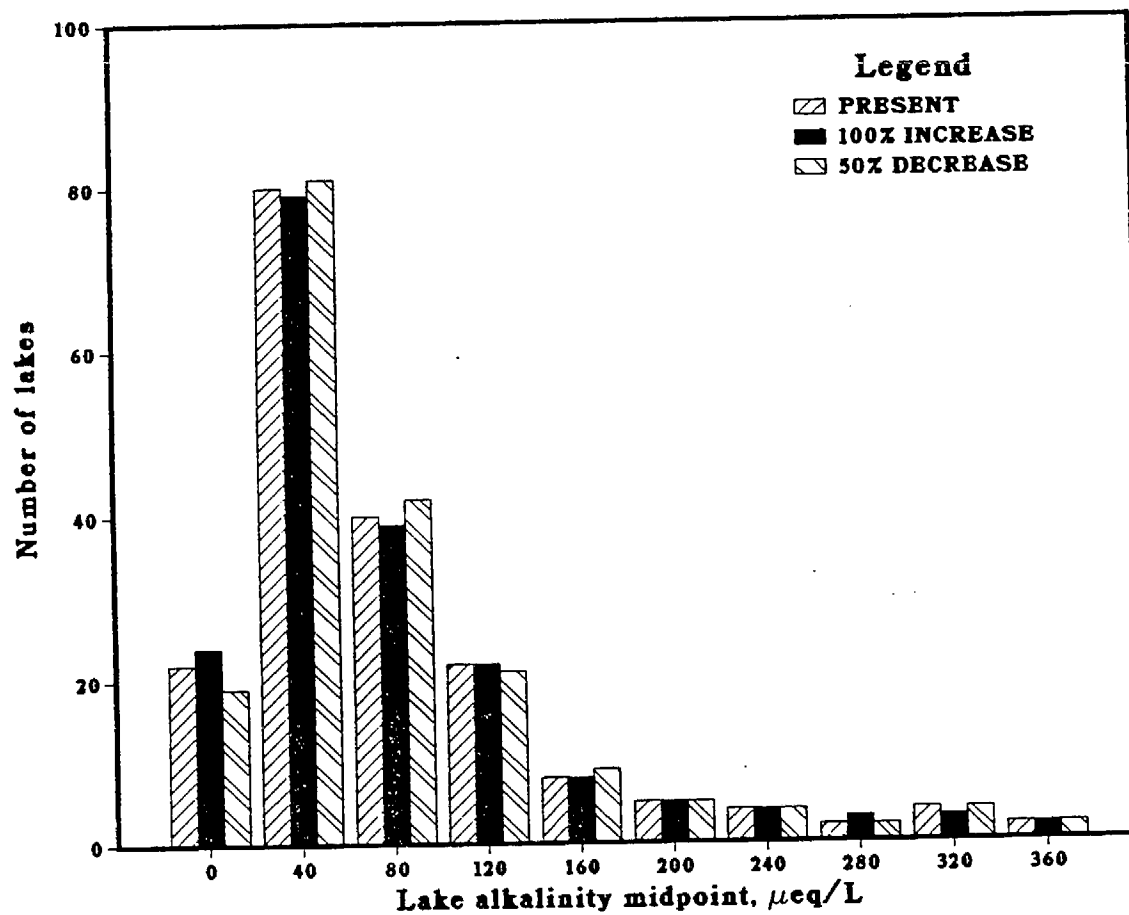
Figure 34. Histogram showing the number of lakes with predicted ANC values using the steady state charge balance model for changes in ammonium nitrate loadings.
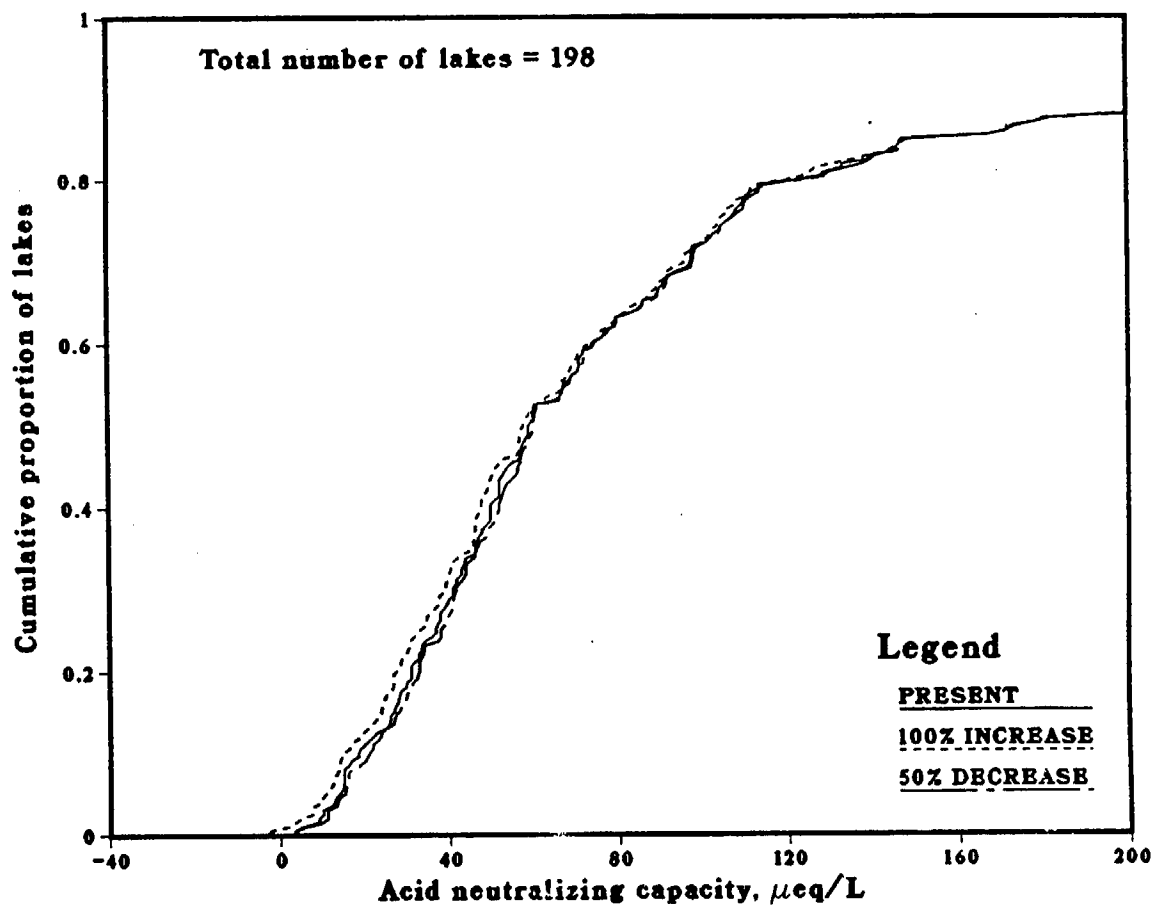
Figure 35.   Predicted chemical condition of UI database lakes due to changes in
             ammonium nitrate loadings in a dry year using the steady state charge
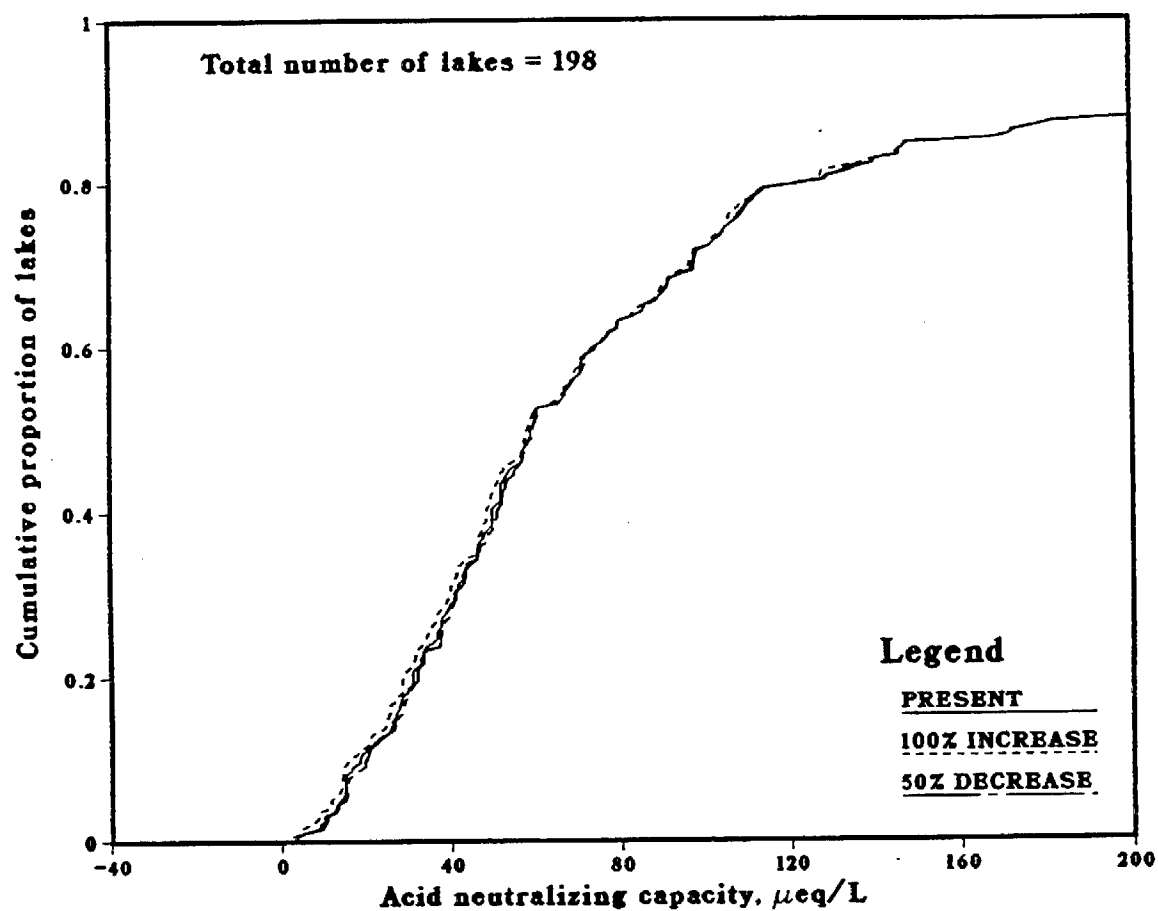   balance model (NH_4^+/NO_3^- = 1:1).

Figure 36. Predicted chemical condition of UI database lakes due to changes in ammonium nitrate loadings in a wet year using the steady state charge balance model (NH_4^+/NO_3^- = 1:1).

ammonium nitrate deposition will rival those of sulfuric acid deposition. This is due to the effect of the biological reactions which take place in the watershed. The results for the case of $NH_4^+/NO_3^- = 1.5:1$ are shown in Figure 37. A 100% increase in current ammonium nitrate loadings under this ratio resulted in 39% sensitive lakes and 4% acidic lakes. The number of sensitive lakes in this scenario increased 8% over that for a 1:1 ratio of ammonium to nitrate. This shows that this ratio will be an important factor in determining the effects on lakes of nitrogen deposition in the future.

Decreases of 50% for this ratio had a greater effect in reducing the percentage of sensitive lakes than for $NH_4^+/NO_3^- = 1:1$. The percentage of sensitive lakes dropped approximately 10% from the present day percentage. This is in contrast to a decrease of 2% for the 1:1 ratio.

The results from the combination of changing both sulfuric acid and ammonium nitrate levels in deposition are shown in Figure 38. These are the results for a normal precipitation year. The effect of changing both of these acid deposition concentrations is an additive effect as shown in Equation 32. This scenario shows the greatest potential for lake acidification under the loadings studied. An increase of 100% of current deposition concentrations results in 37% of the lakes becoming sensitive to further inputs of acid. More importantly, 3% of the lakes will become acidified under this loading increase. Half of the current deposition levels of sulfuric acid and ammonium nitrate result in 22% sensitive lakes. This scenario shows the greatest impact on decreasing the number of sensitive lakes through decreased acid loadings. Figure 39 shows the results for this scenario in histogram format. The effect of the changes in acid loadings studied are most evident in the -20 to 20 μeq/L (0 alkalinity midpoint) range. The number of lakes in this range just about doubles for a 100% increase in acid loading. A decrease in acid of 50% results in less than half the number of currently sensitive lakes.
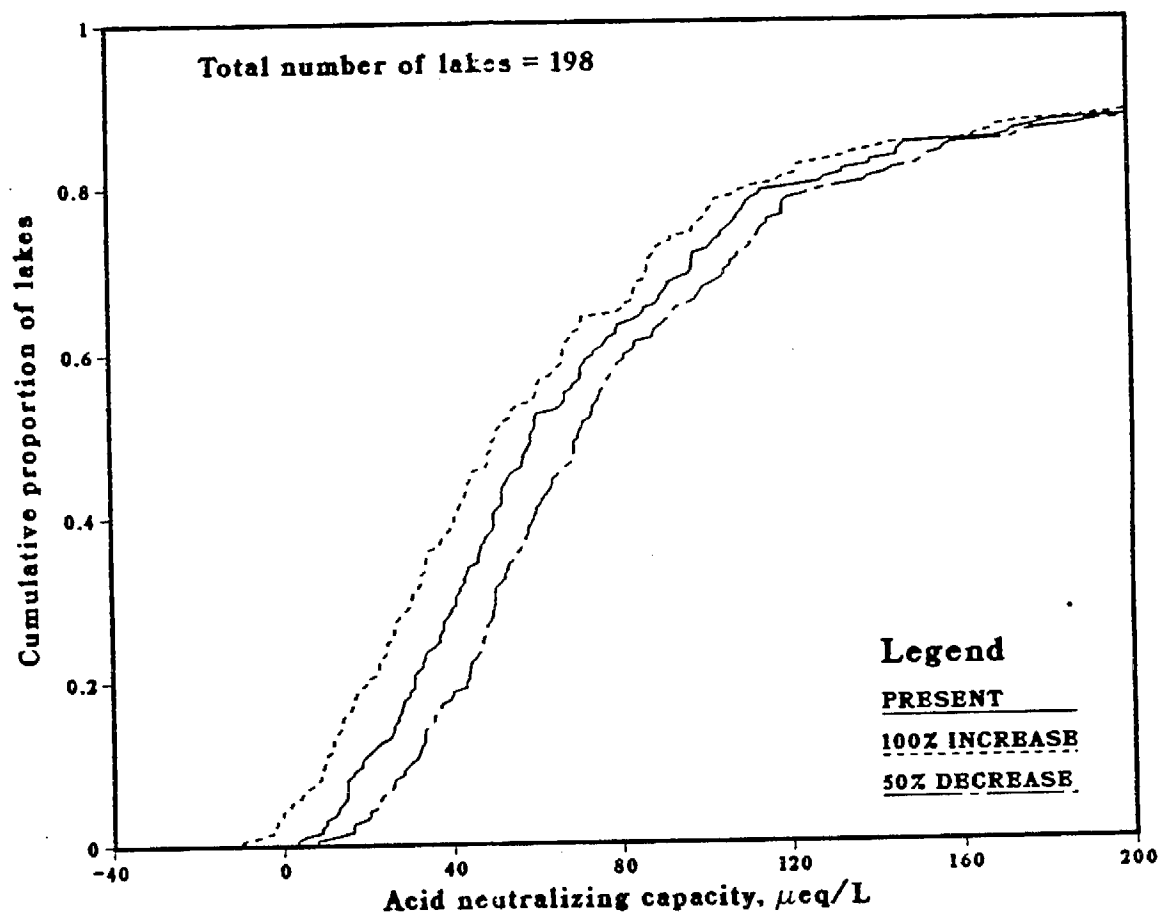
Figure 37. Steady state charge balance model predicted chemical condition of UI database lakes due to changes in ammonium nitrate loadings for $NH_4^+/NO_3^- = 1.5:1$.
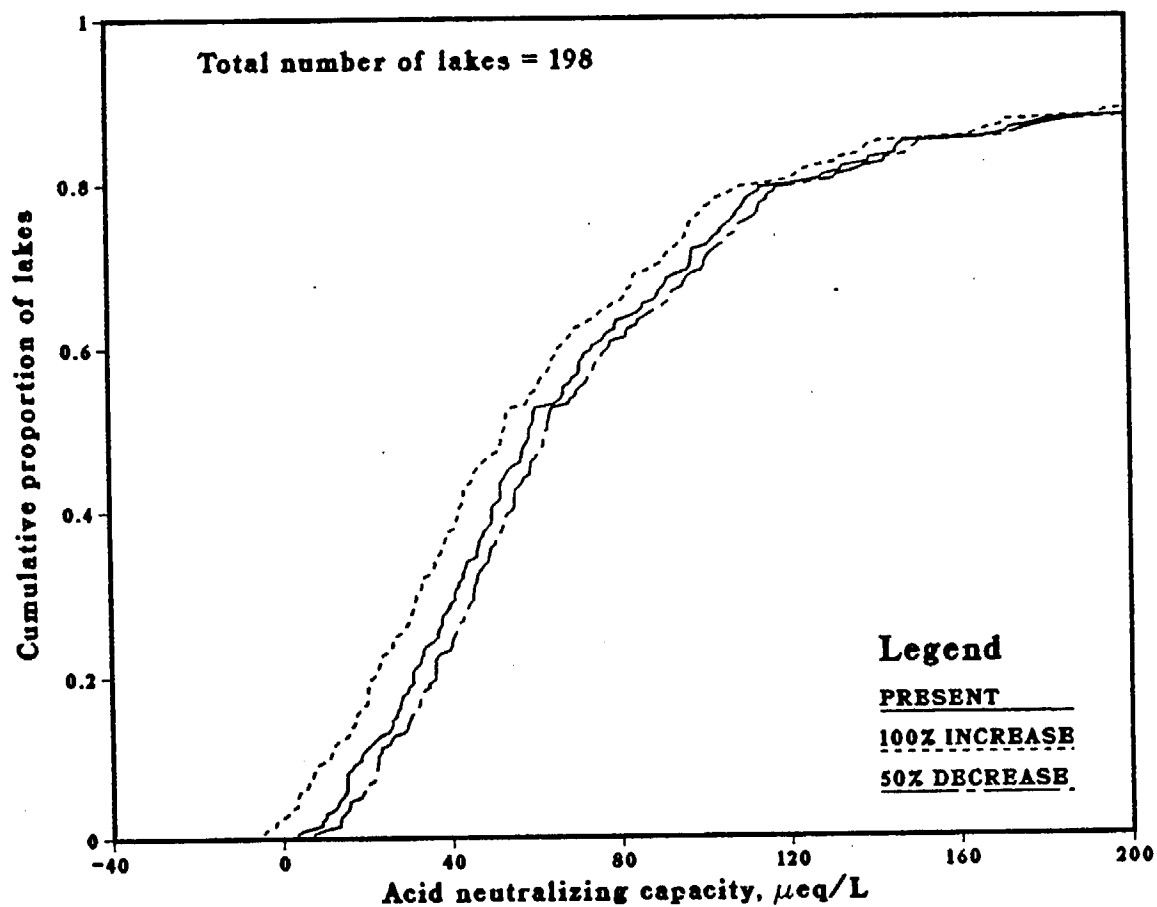
Figure 38.   Steady state charge balance model predicted chemical condition of UI database lakes due to changes in sulfuric acid and ammonium nitrate loadings (F=0.4 and $NH_4^+/NO_3^- = 1:1$).
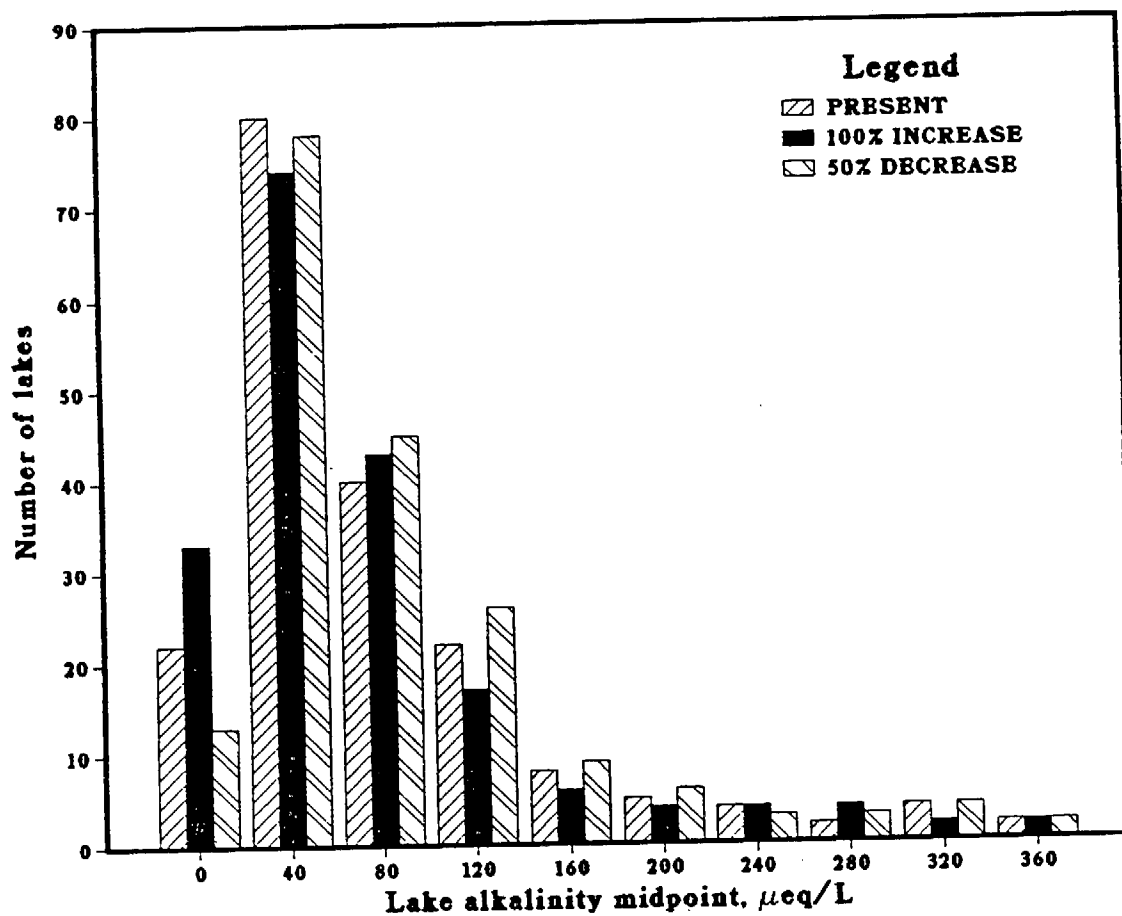
Figure 39.   Histogram showing the number of lakes with predicted ANC values
using the steady state charge balance model for changes in ammonium
nitrate and sulfuric acid loadings.

The results for a low precipitation year are shown in Figure 40. As shown in the previous scenarios, this case has a greater effect on the number of sensitive lakes under each loading. Doubling the current levels of deposition sulfuric acid and ammonium nitrate results in 39% sensitive lakes. The number of acidic lakes (3%) is the same as for the case of a normal precipitation year. Decreases in acid loadings result in only 23% of the lakes being sensitive to further acid loadings in a dry year.

Changes in acid loadings have a less pronounced effect in wet years than in normal precipitation years. The results for a wet year case are shown in Figure 41. An increase of 100% in current deposition values of sulfuric acid and ammonium nitrate results in 34% sensitive lakes while a decrease of 50% shows that 23% of the lakes will remain sensitive.

Figure 42 shows the results for the same scenario but with $NH_4^+/NO_3^- = 1.5:1$. The change in the percentage of sensitive lakes is much more drastic in this case. Increases of 100% in deposition loadings resulted in 43% sensitive lakes with 7% of the lakes becoming acidic. The number of sensitive lakes under a 50% decrease in loadings was 15%, a drop of almost 14% from the current percentage.

Sensitivity Analysis

The two critical parameters in this model are the evapoconcentration factor and the Henriksen F-factor. A sensitivity analysis based on these two parameters was performed to determine their effects on predicted ANC. It is probable that there are some uncertainties in the values of lake and deposition chemsitry as well. However, additional data are required to perform a detailed sensitivity analysis based on these parameters. This is addressed in the Recommendations section in the next chapter.

As stated previously, the evapoconcentration factor was estimated for each lake by using the sulfate concentration in the lake and in precipitation. This is not an altogether safe
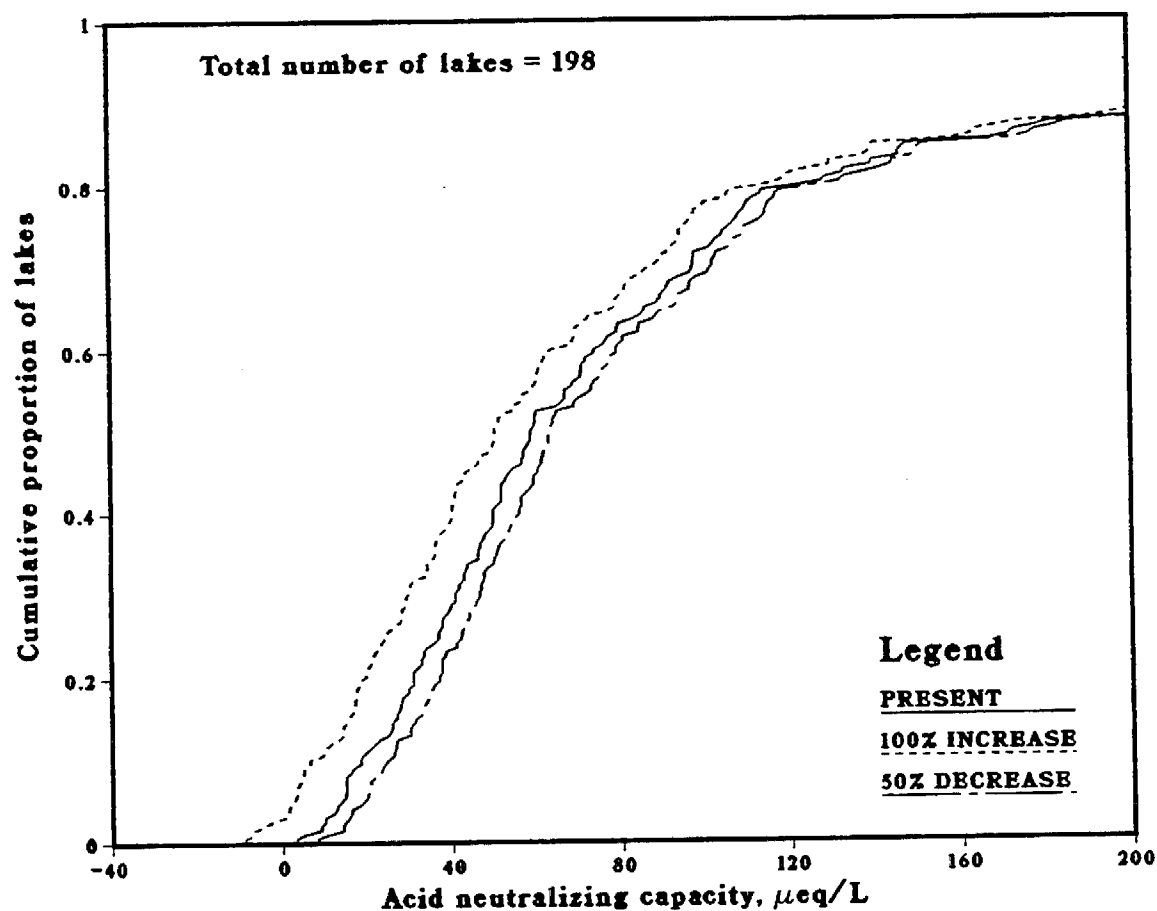
Figure 40. Predicted chemical condition of UI database lakes due to changes in ammonium nitrate and sulfuric acid loadings in a dry year using the steady state charge balance model ($NH_4^+/NO_3^- = 1:1$).